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INTERAGENCY FLUE GAS DESULFURIZATION EVALUATION FINAL REPORT

by

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16. ABSTRACT

The report gives results of a 6-month study of flue gas desulfurization (FGD) technology conducted by an interagency team in 1977. The study was mandated by President Carter in his April 1977 National Energy Plan. The purpose of the study was to determine whether additional Federal funding would accelerate the commercialization and acceptance of FGD technology. The report concludes that FGD is the most viable short-term approach to meeting increased coal-use objectives of the National Energy Plan, and it identifies specific FGD research, development, and demonstration priorities. The report also presents a background of FGD technology (as of 1977) and the methodology used in the study to select the most promising FGD processes and subsystems. The appendices give detailed technical data on specific FGD technology.

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Desulfurization		07A,07D
Coal		21D
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ABSTRACT

This report presents the results of a six-month study of flue gas desulfurization (FGD) technology conducted by an interagency team in 1977. The study was mandated by President Carter in his April 1977 National Energy Plan (NEP). The purpose of this study was to determine whether additional Federal funding would accelerate the commercialization and acceptance of FGD technology. This report concludes that FGD is the most viable short-term approach to meeting increased coal-use objectives of the NEP, and it identifies specific FGD research, development, and demonstration priorities. This report also presents a background of FGD technology (as of 1977) and the methodology used in the study to select the most promising FGD processes and subsystems. The appendices provide detailed technical data on specific FGD technology.

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1.0 INTRODUCTION

Flue gas desulfurization (FGD) technology is recognized as the most viable approach to the environmentally acceptable direct use of coal in the near term. Indirect coal utilization, primarily in the form of coal liquefaction or gasification products, will be an important option in the 1990's--as well as fluidized bed combustion, a form of direct coal utilization not yet commercially demonstrated for large boilers.

In April 1977, President Carter presented his National Energy Plan (NEP) which was based, in large measure, on the increased use of coal. The NEP stated that, in the short term, most coal will continue to be burned directly and thus, the highest immediate priority is the development of more effective, economical methods to meet air pollution control standards.

Accordingly, one of the specific elements in the President's plan was a "six-month review" to determine which, if any, FGD technologies under development offered sufficient environmental, cost, and reliability advantages to merit an accelerated research, development, and demonstration (RD&D) program.

In response to this mandate, an "Interagency Flue Gas Desulfurization Evaluation Study" was initiated as an internal study to guide government RD&D and help accelerate the application of technology. A draft report was produced in late 1977. Although a variety of circumstances have delayed publication of the final report, the methodology developed as part of this study is still useful in comparing and evaluating processes at different stages of development. Also, the interagency FGD study has been widely used in shaping government funding priorities for FGD research and development. It also provides useful data and conclusions regarding the prospects of near-term progress in improving FGD efficiency, reliability and costs.

Thus the major conclusions of this study remain valid, even if some of the material is dated. In fact, the need to bring new FGD systems and processes on-stream is even more pressing today than it was in 1977. During the period from 1977-1979, several developments occurred that underscore the need for increased coal utilization over the short term and continued progress in reducing emissions from coal combustion. These include the promulgation of more stringent new source performance standards for utility boilers, the disruption of foreign crude oil supplies and sharp increases in OPEC oil prices, the enactment of legislation prohibiting the use of oil and gas in many new utility and industrial facilities, and the growing uncertainty of nuclear energy.

Section 2.0 presents the basic conclusions of the study, Section 3.0 sets out specific FGD research, development, and demonstration recommendations of funding priorities and levels. Section 4.0 provides an overview of future coal use, a status report on FGD technology, and background information on alternative coal use options. Section 5.0 describes the approach used by the interagency study group to evaluate FGD technology.

2.0 CONCLUSIONS

The principle conclusions of this study were that.

- There are significant potential benefits to be derived from increasing the level of Federal funds for Flue Gas Desulfurization Research, Development, and Demonstration (FGD RD&D) efforts.
- Increased Federal funding should be used for research and development projects to improve systems, both throwaway and regenerable, that have been or are being demonstrated on large-scale equipment.
- Resources should be available for process and subsystem evaluations of potential solutions to common FGD problems and new developments in FGD technology.

This study also concluded that application of further government funding to FGD research has the potential for:

- Improvement of current commercial processes in the areas of economics, process reliability, technical viability, energy usage, and environmental acceptability.
- Development of new processes that are superior to current commercial processes in applicability, ability to meet regional or site specific needs, and energy and economic characteristics.

3.0 RECOMMENDATIONS

The most effective way to advance FGD technology would be through RD&D funding to find near-term solutions to problems faced by commercial and near-commercial processes. A secondary priority should be assigned to processes and process developments that provide longer-term benefits. To meet both of these objectives, the following recommendations were developed:

1) Lime/Limestone Improvements

A. Mass Transfer Additives - An extension of current programs that have focused upon evaluating magnesium as a mass transfer additive for lime/limestone processes was recommended. Specific additives to be examined include both organic and inorganic chemicals such as adipic acid and sodium carbonate. The use of such additives has the potential for improving the SO_2 removal ability of lime/limestone systems, increasing sorbent utilization, and decreasing process costs. Thus the primary benefits of this research could result in increased application of lime/limestone FGD technology and a lower process cost. Initial efforts should be pilot-scale testing followed by a prototype demonstration unit.

B. Forced Oxidation - EPA has an existing program at TVA's Shawnee Steam Plant. Pilot testing of two process variations is currently being conducted. A full-scale demonstration program was recommended for 1979-1980. A full-scale demonstration of this concept could benefit lime/limestone technology in reducing sludge disposal problems, thus removing a major environmental impediment to lime/limestone scrubbing and increasing its applicability. In addition, a potentially marketable gypsum product may be produced. Full-scale demonstration could occur by modifying an existing system. This appears to be the next step in commercializing the technology.

C. Contactors - Extension of current work on cocurrent scrubbing was recommended. Demonstration of a 100 MW prototype cocurrent scrubber could significantly reduce cost and complexity of lime/limestone scrubbing, and extension and expansion of current programs appears necessary to conclusively answer operability questions.

In addition, testing and demonstration of the Chiyoda 121 system was recommended because this system has claimed significant cost reductions over conventional limestone scrubbing due to its simple design.

D. Sludge Disposal - Extension of current sludge disposal activities to evaluate large-scale disposal options (fixation, lining, and ponding) was recommended. Sludge disposal is a major environmental problem in lime/limestone scrubbing. Resolution of this problem at a large scale could enhance the applicability of the lime/limestone and double alkali systems.

E. Hardware Improvements - Problems with instrumentation, mist eliminators, reheaters, and stack liners have been the cause of recent FGD system failures. Additional development work to improve these components was recommended as a means of increasing the reliability and operability of wet FGD systems. Demonstration of the improved designs on full-scale systems was recommended to encourage their acceptance by the industry.

2) Sulfur Production with Carbon

A. RESOX - EPRI is funding a RESOX demonstration program in Germany to produce sulfur from the Bergbau-Forschung FGD unit using anthracite as the reductant. Recommendations included evaluation of the RESOX process in a demonstration-sized facility with feed from other front-end systems, and evaluation of coals other than anthracite for use as a reductant. The overall applicability of the RESOX process suffers because it has not been evaluated on other systems. Extension of the EPRI program to test the RESOX process under different conditions could result in the solution of a major problem in FGD: sulfur production without the use of a reducing gas. This could significantly enhance applicability of FGD due to its potential for reducing cost, complexity, and secondary pollution.

B. Rockwell International Molten Carbonate Regeneration - Extension of the EPRI program to demonstrate and operate the RI Regeneration System in an integrated mode to gather data for full-scale design and construction was recommended. RD&D efforts on this system would demonstrate direct conversion of SO_2 to sulfur without a reducing gas and would provide additional design data for the ACP process to be constructed at Niagara Mohawk with government support.

3) Continuing Evaluation Effort - Funds should be set aside for technical and economic evaluations of specific process problems or of future processes that may offer advantages over current FGD technology. This would assure that future improvements in FGD technology are given a complete and timely evaluation. In addition, it would provide a source of funding for studies on critical issues in FGD technology that could be of significant benefit in directing future RD&D efforts.

4) Magnesia Slurry Scrubbing - Demonstration of sustained sulfuric acid production from a full-scale system was recommended. In addition, demonstrating the ability to produce sulfur directly in the calciner would significantly enhance process applicability. Both concepts should be demonstrated and evaluated on a full-scale system.

5) Limestone Use in Double Alkali Systems - Demonstration of the use of limestone as the regenerant in ongoing pilot work, and extension and modification of the EPA-sponsored demonstration program at LG&E to test limestone was recommended. The use of limestone in double alkali systems has the potential for significantly improving the system operating costs because limestone is a less expensive raw material than lime.

6) Sodium Sulfite System Waste Handling

A. Disposal - Tests of fixation concepts plus other methods of sludge handling and disposal from once-through sodium sulfite systems was recommended. The disposal of sodium sludge is a major problem in the sodium-based throwaway processes. Solution of this would increase the applicability of the processes and provide potential reductions in cost and environmental impact.

B. Regeneration - Evaluation and eventual testing of methods for regeneration of sodium sulfite system by-products was recommended. This would have a similar benefit to the option listed above: it could eliminate the disposal problems faced by sodium sulfite systems and reduce raw material costs.

7) Application of Low-Btu Gas - Evaluation of the application of coal-derived low-Btu gas as a reductant in FGD systems was recommended. This would include feasibility studies to evaluate system requirements, followed by demonstrations of the application of specific gasification systems. The use of coal gasification could eliminate the dependence of some regenerable FGD processes on increasingly costly and scarce supplies of natural gas.

8) Sorption/Steam Stripping - Extension of EPRI laboratory studies and pilot work, to be followed by demonstration at the 60-100 MW level, was recommended. The design of a general test facility for testing the large number of systems currently under consideration would be beneficial. The Sorption/Steam Stripping concept appears to have potential for more reliable, lower cost operation than some other regenerable systems and should be evaluated.

9) Dowa Test Facility - A pilot plant program to evaluate the feasibility of the Dowa Process for coal-fired applications should be established. The process received high evaluations and appears to have significant advantages over current double alkali FGD technology because it uses limestone as a regenerant and produces a marketable quality gypsum by-product. A similar program is, however, currently being planned by EPRI and TVA.

10) Integrated Cat-Ox - Additional support for the Cat-Ox Process was recommended to demonstrate the Integrated Cat-Ox System at the 100 MW level. The Integrated Cat-Ox Process has shown significant cost advantages over current FGD technology. Development of the process could produce significant reductions in both costs and process complexity.

11) SULF-X - An evaluation of the SULF-X Process to independently analyze vendor claims was recommended. The

process has potential as a SO_x/ NO_x flue gas treatment process. This evaluation is currently being undertaken by DOE.

The Working Group developed and recommended funding levels that would be necessary to pursue each of these RD&D opportunities. These estimates are shown in Figure 3-1. Historically, funding for major FGD demonstration efforts has been on a cost-shared basis with the process vendor and/or the host. It is anticipated that the RD&D programs recommended above would in all likelihood be funded on a cost-sharing basis with industry, EPRI, or state and local governmental agencies. The estimated RD&D costs shown in Figure 3-1 are estimates for completing the total recommended program. The Working Group did not attempt to define percentage funding by participant. Table 3-1 presents a summary of the recommended RD&D opportunities with benefits expected and scheduling. The consensus of the Working Group was that these research opportunities be funded based on the ranking shown in Figure 3-1.

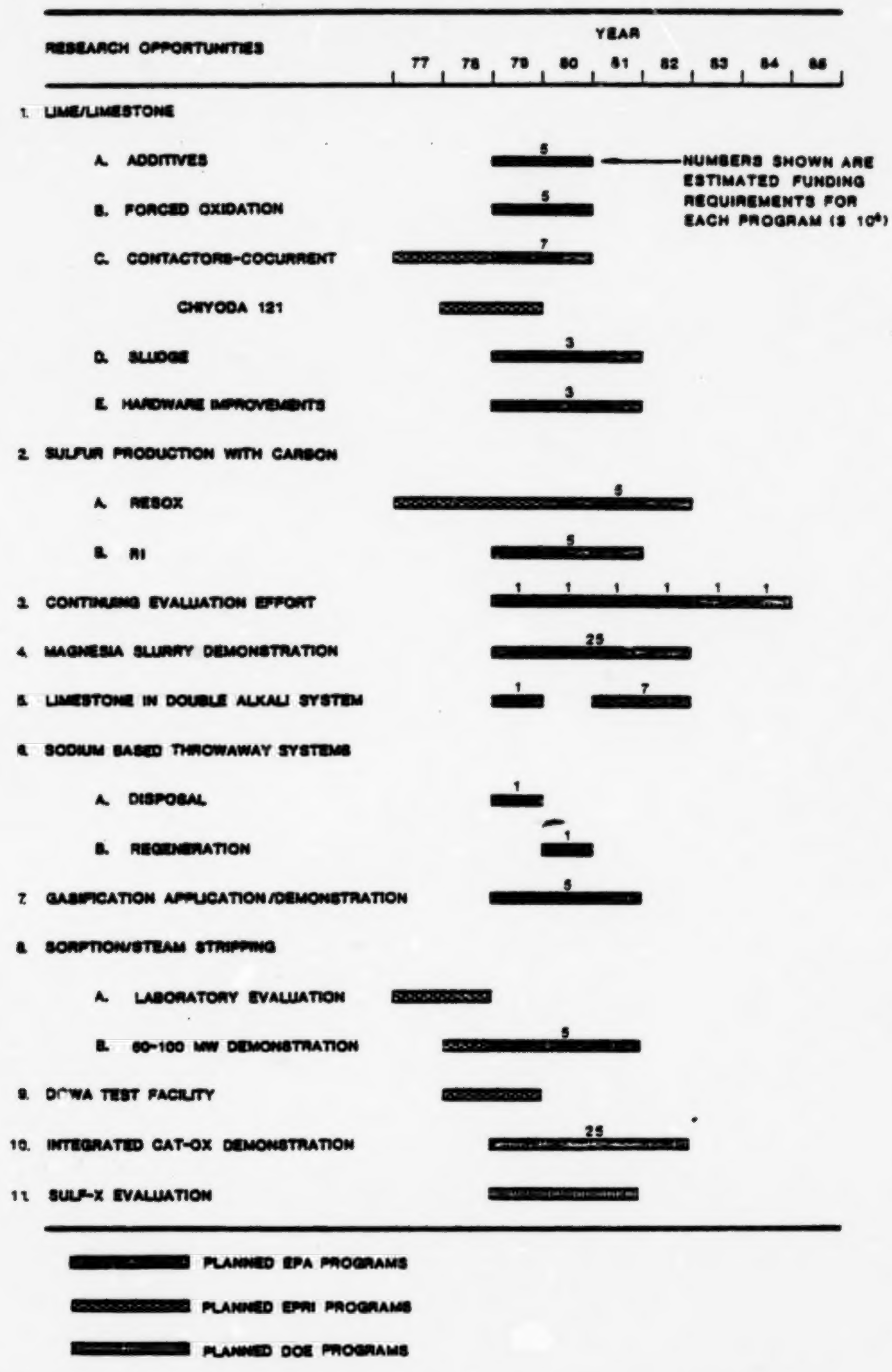

Figure 3-1. RD&D Priority List - Schedule and Costs.

TABLE 3-1. RANKING OF RECOMMENDED RD&D OPTIONS IN FLUE GAS DESULFURIZATION

RD&D Option	Proposed Project	Benefit Expected	Schedule
Lime/Limestone Improvements			
A. Additives	Extend current programs to pilot and full-scale demonstration investigations of organic additives.	Improved mass transfer leading to lower costs, better limestone utilization, simplified scrubber design, and better operation.	1979-1980
B. Forced Oxidation	A full-scale demonstration unit was recommended for 1979-1980.	Improved sludge quality leading to easier disposal with fewer environmental effects and a potentially marketable gypsum by-product.	1979-1980
C. Contactors	Continue work on cocurrent contactors and the Chiyoda 121 Process. A test should be undertaken to determine the ability of lime/limestone scrubbing to meet reduced SO_2 emission standards.	Cocurrent scrubbing can lead to simpler scrubber design and better system operation. The Chiyoda 121 Process could be a simpler, less expensive and more easily operated limestone system.	1979-1980
D. Sludge Disposal	Conduct large-scale evaluation of disposal options such as fixation, lining, and ponding.	Improved sludge disposal would increase environmental acceptability of lime/limestone and double alkali systems.	1979-1981
E. Hardware Improvements	Improve mist eliminators, reheaters, stack liners, and other equipment contributing to FGD system failures.	Demonstration of improved hardware designs would improve operating reliability and expedite acceptance by industry.	1979-1981
Direct Sulfur Production With Carbon			
A. RESOX	A commercial-scale RESOX installation with feed from systems other than Bergbau Forschung and use of coals other than anthracite should be evaluated.	Direct reduction with carbon would be a less expensive and more acceptable method of sulfur production than use of scarce, expensive natural gas or use of a reducing gas produced from a coal gasification process.	1980-1982

TABLE 3-1. RANKING OF RECOMMENDED RD&D OPTIONS IN FLUE GAS DESULFURIZATION (Continued)

RD&D Option	Proposed Project	Benefit Expected	Schedule
B. RI	Integrated piloting of the RI ACP System was recommended.	Data from full scale demonstration and integrated operation would be gathered.	1977-1980
Continuing Evaluation Effort	Funds should be set aside for technical and economic evaluation of general FGD problems and of processes that, in the future, may offer advantages over current FGD technology but which were not considered in this study due to their lack of development.	There are many common problems in FGD technology (materials of construction, reheat, etc.) which are not tied to any given process. Thus, work in this area would benefit FGD technology as a whole. In addition, new developments in FGD technology will be monitored.	1979-1984
Magnesia Slurry Process	Sustained sulfuric acid production and sulfur production in the calciner should be demonstrated at full scale (greater than 100 MW) level.	Demonstration at 100 MW is a crucial step in commercialization. Integration of the Magnesia Slurry scrubbing process with an acid or sulfur production unit is critical to process commercialization and acceptance.	1979-1982
Limestone Utilization in Double Alkali Systems	Limestone regeneration in on-going pilot work and at large scale (perhaps at Cane Run) should be demonstrated.	Use of limestone rather than lime in double alkali systems could lower overall process costs.	1979, 1981-1982
Sodium Sulfite System Improvements			
A. Disposal	Fixation and other methods of sludge handling and disposal from once-through sodium sulfite systems should be tested.	Development of a means of disposing of sodium sulfite sludge in an environmentally acceptable manner would eliminate a major constraint on system applicability.	1979
B. Regeneration	Evaluation of methods for regenerating sodium sulfite systems scrubbing media was recommended.	Regeneration of spent sodium sulfite/sulfate could reduce raw material absorbent costs and eliminate disposal problems.	1980

TABLE 3-1. RANKING OF RECOMMENDED RD&D OPTIONS IN FLUE GAS DESULFURIZATION (Continued)

RD&D Option	Proposed Project	Benefit Expected	Schedule
Coal Gasification to Produce a Reducing Gas	Demonstration of the application of coal gasification-produced low-Btu gas to FGD systems was recommended.	Application of coal gasification to reducing gas production and utilization in FGD systems could eliminate dependence on increasingly unavailable and costly natural gas and naptha.	1979-1981
Sorption/Steam Stripping Demonstration	Laboratory studies, pilot work, and demonstration at the 60-110 MW level were recommended.	The concept of sorption/steam stripping offers potential advantages in process simplicity, energy use, and costs in application to FGD processes.	1979-1981
Dowa Process	A pilot plant program to evaluate Dowa Process feasibility in coal-fired applications was recommended.	The Dowa Process ranked high in the Working Group evaluation. Although commercially demonstrated on oil-fired units in Japan, it needs to be demonstrated on a coal-fired unit.	1977-1979
Integrated Cat-Ox Demonstration	Demonstration of the Integrated Cat-Ox System at the 100 MW level was recommended.	The Integrated Cat-Ox Process shown potential cost advantages over other FGD processes. Demonstration of this process is required for commercialization.	1979-1982
SULF-X Evaluation	The SULF-X Process should be independently analyzed to evaluate vendor claims.	Claims of process potential need to be evaluated.	1979-1981

4.0 BACKGROUND*

This study was directed by the President as a review of FGD technology to identify research options that could accelerate commercialization of FGD. In this section, a projected increase in coal consumption is presented based upon the implementation of the 1977 National Energy Plan. Then the impact of this increased coal consumption is assessed, the status of FGD technology (in 1977) summarized, alternatives (to FGD technology) for controlling SO_2 emissions addressed, and a brief description of existing and planned government and EPRI FGD RD&D programs (as of 1977) presented.

In summary, this background section illustrates the following two points:

1) FGD technology will remain the primary alternative for controlling SO_2 emissions from 1978-1985.

2) There are problems with existing FGD technology that must be resolved for it to achieve greater acceptability.

The discussion of current and planned FGD RD&D programs (as of late 1977) provided a basis for investigating benefits that could be obtained from additional RD&D projects.

4.1 Projected Increase in Coal Consumption

Since the early 1970's, U.S. energy policy has focused on the goal of reducing the country's reliance on dwindling reserves of natural gas and costly supplies of foreign oil. This policy has gradually increased the use of coal as a primary energy source in this country. The 1977 National Energy Plan (NEP) was designed to accelerate the increase in coal utilization. The goal of the program was to increase projected coal consumption in 1985 by approximately 200 million tons above levels of coal usage predicted without the NEP. The program seeks to encourage coal use by:

- Escalating taxes for continued use of oil and natural gas,
- Granting tax credits or rebates for coal-handling and coal combustion equipment,

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*Note: As previously noted, this report is based on the situation found in 1977 and its background.

- Allowing a gradual rise in wellhead oil and gas prices, and
- Prohibiting, with certain exceptions, all new utility and industrial boilers larger than 10 MW from burning oil or gas fuels.

The projected effect of the NEP will be to increase total coal consumption in 1985 by about 20 percent over the 1985 base levels (Table 4-1). The most dramatic increase will occur in the industrial sector, where coal use is expected to triple over the 1985 base levels.

TABLE 4-1. PROJECTED UTILITY AND INDUSTRIAL DEMAND FOR COAL (Millions of Short tons) (Ref. - US-790)

	1975 Actual	1985[2] Base Level (Without NEP)	1985[1] (With NEP)	1985 Increase in Demand Generated by NEP	Percentage Increase in Demand over 1975 resulting from NEP
Utility	404	763[3]	779	16	92.8%
Industrial[3]	63	101	278	177	341.3%
Total	467	864	1057	193	126.3%

[1] Includes effects of the coal program and conservation policies.

[2] FEA Project Independence model (PIES) run A148524C.

[3] Does not include metallurgical coal.

4.2 Projected Sulfur Dioxide Emissions under the National Energy Plan

Projected utility and industrial SO emissions, including baseline emissions for 1985 (without accelerated coal utilization) and project emissions assuming implementation of the NEP, are presented in Table 4-2. These predictions contain uncertainty due to possible errors in predicting fuel switching, fuel usage growth, regulatory environment, and other factors. However, the data presented in the table represented a reasonable prediction based upon the information available in 1977. Emission estimates were constructed under two regulatory scenarios. The first (compliance with current standards) assumed that:

- All sources will be governed by present SO_2 emission regulations through 1985.
- Full compliance with these regulations will be achieved by 1985.

The second scenario (use of Best Available Control Technology--BACT) assumed that:

- BACT will achieve 80% SO_2 emission reduction as a result of 90% removal efficiency with 90% availability on locally available coal.
- BACT will be applied to all new utility sources after 1984, and all new industrial sources after 1979.
- A revised NSPS of 1.5 lb $SO_2/10^6$ Btu for small sources (10-25 MW) will be promulgated.
- Existing sources regulated by State Implementation Plans (SIP's) will reach full compliance by 1985.

Under the first scenario (current standards), the NEP would result in a 5% increase in SO_2 emissions over the 1985 baseline and a 16% increase over actual 1975 emissions. Federal NSPS are a reflection of the adequately demonstrated emission control possible through the use of the best available technology. However, considering recent improvements to FGD technology and the revised amendments to the Clean Air Act, it was considered likely that more stringent standards would be promulgated before 1985. This first regulatory scenario was presented, then, not as a prediction of the future, but as an indication of the SO_2 emissions that would result from implementing the NEP with current standards.

Under the second scenario (BACT), the NEP would result in only a 2% increase over total 1975 SO_2 emissions and a net 3% reduction in emissions over the 1985 baseline. This reduction from the 1985 baseline is primarily due to the President's energy conservation policies (as evidenced by the 9% reduction in utility emissions compared to the baseline) which offset the effects of fuel switching. This analysis indicates that, given a broad application of BACT, the NEP would result in a net reduction in emissions forecasted for 1985, despite the major increase in coal consumption brought about by the oil and gas replacement policy.

While this analysis addresses SO_2 emissions on a national basis, the environmental impact of the coal conversion program will also have to be assessed regionally. In areas which currently rely heavily on oil and natural gas for power production, the switch to coal could significantly increase local SO_2 emissions with resultant increases in ambient SO_2 levels. And because of the larger percentage increase in industrial coal usage, heavily industrialized areas may experience a greater impact from SO_2 emissions than the national average. Therefore, the decision as to what constitutes adequate SO_2 control must be made on a regional basis in order to insure that the goal of preserving existing air quality is met.

TABLE 4-2. UTILITY AND INDUSTRIAL SO_2 EMISSIONS
(Millions of Tons per Year) (US-790)

	1975 Actual	1985 Baseline	1985 President's Program	Percentage Change Over 1985 Baseline
Compliance with Current Standards[1]				
Industry	10.8	12.4	15.9	(+28%)
Utility	18.6	20.2	18.2	(-10%)
Total	29.4	32.6	34.1	(+5%)
Use of Best Available Control Technology (BACT)[2]				
Industry	10.8	10.8	11.7	(+8%)
Utility	18.6	20.2	18.3	(-9%)
Total	29.4	31.1	30.1	(-3%)

[1] Assumes full compliance with current standards by 1985: NSPS for new large boilers and SIP's for new small (10-25 MW) boilers: SIP's govern existing sources not subject to NSPS.

[2] Assumes BACT applied to all new utilities which begin operation after 1974 and to new industrial sources, after 1979.

4.3 Compliance with Present and Future Sulfur Dioxide Standards

In 1975, EPA published a report evaluating the compliance status of coal-fired power plants (EN-629). This report stated that, in 1974, roughly 50% of the coal was burned by utility boilers that were in compliance with existing SO_2 emission regulations. The remainder was burned at plants falling into one of the following categories:

- Involved in environmental litigation (22%).
- Not in compliance, but with plans for achieving compliance submitted to EPA (12%).
- Not in compliance, plans unknown (17%).

It was apparent then, that the nation was far from achieving complete compliance with existing regulations, even though the vast majority of sources were regulated by SIP's.

The EPA report, which did not include the impact of the NEP in increasing coal utilization, also investigated projected compliance status through 1980. This analysis concluded that, by 1980, 40% of the total coal demand by utilities will come from plants constructed after 1974. Of this 40%, 10% will be consumed by facilities operational in 1975 and 1976 (thereby subject to SIP's), and 30% (or 185 million tons out of an estimated 625 million tons) will be consumed by sources coming online after 1976 and thereby regulated by the Federal NSPS. By comparison, only 1.5% of the major sources identified by EPA's Compliance Data System in April 1976 were subject to Federal standards (EN-630). Thus, the number of plants falling under NSPS and under requirements for FGD can be expected to increase significantly.

The Federal NSPS for SO_2 emissions from coal-fired boilers was designed "to reflect the degree of emission limitation achievable through the application of the best system of emission reduction...which has been adequately demonstrated" (EN-630). Since many people feel that commercial scrubbing systems are now capable of meeting NSPS, it can be assumed that, as this technology develops, regulatory legislation will require more stringent standards. Table 4-3 shows the amount of SO_2 removal necessary with high, medium, and low sulfur coals to comply with the current (1977) standard and two tighter standards. The Clean Air Act Amendments of 1977 did not specify the value for new SO_2 standards and, therefore, two more stringent potential levels of control were selected for comparison.

TABLE 4-3. % SO_2 REMOVAL NECESSARY TO COMPLY WITH STANDARDS[1]

	Current Standard 1.2 lbs $SO_2/10^6$ Btu	Potential Standard 0.8 lbs $SO_2/10^6$ Btu	Potential Standard 0.4 lbs $SO_2/10^6$ Btu
High Sulfur Coal (5% Sulfur; 10,500 Btu/lb)	86.7%	91.2%	95.6%
Medium Sulfur Coal (3.5% Sulfur; 10,500 Btu/lb)	81.1%	87.4%	93.7%
Low Sulfur Coal (0.8% Sulfur; 8,000 Btu/lb)	36.8%	57.9%	78.9%

[1] Using SO_2 emission factors found in "Compilation of Air Pollutant Emission Factors, Second Edition" AP-42, February, 1976.

In summary, the number of sources governed by Federal NSPS will increase significantly between 1976 and 1985, since most of the increased coal use projected to occur within this time will occur in new or replacement facilities that will be subject to NSPS. The possibility of tighter standards and the planned increase in the consumption of coal, coupled with this increase in the number of sources governed by Federal NSPS, point to a greater utilization of SO_2 control devices in the years to come. The next section discusses the current availability of FGD and its ability to meet future needs.

4.4 Present Status of Flue Gas Desulfurization in the United States

As of June 1977, there were a total of 119 FGD units including 7,800 MW of FGD capacity which EPA considered operational, 12,600 MW under construction, and 30,000 MW planned (Table 4-4). This was a total potential scrubbing capacity of roughly 51,000 MW out of a total coal-fired generating capacity of 275,000 MW (PE-282).

All of these 119 FGD units were designed for coal-fired sources. Eighty-four or 70% of these units were new installations, and thirty-five (30%) were retrofit installations. Over 90% of the FGD systems that were operational or under construction in 1977 employed some variation of the lime/limestone scrubbing process which produces a sludge that must be disposed of.

TABLE 4-4. SUMMARY OF FGD SYSTEMS BY PROCESS
(MW Capacity)

Process	Operational	Under Construction	Planned				Total Capacity
			Contract Awarded	Letter Of Intent	Requesting/ Eval. Bids	Considering FGD System	
Lime Scrubbing	2702	4158	2350	0	0	660	9870
Lime/Alkaline Fly Ash (Process Not Selected)	0	0	0	527	0	0	527
Lime/Alkaline Fly Ash Scrubbing (Process Not Selected)	720	450	1400	500	0	450	3520
Lime/Limestone Scrubbing (Process Not Selected)	20	0	0	0	0	0	20
Limestone Scrubbing	3767	6750	4911	0	545	1630	17603
Subtotal-Lime/Limestone	7209	11358	8661	1027	545	2740	31540
Aqueous Carbonate Scrubbing	0	0	100	0	0	0	100
Double Alkali Scrubbing	0	575	527	0	0	0	1102
Magnesium Oxide Scrubbing	120	0	0	240	0	486	846
Not Selected	0	0	0	0	3020	10480	13500
Regenerable Not Selected	0	0	0	500	0	1150	1650
Sodium Carbonate Scrubbing	375	0	509	125	0	0	1009
Wellman-Lord/Allied Chemical	115	715	0	0	0	0	830
Citrate	0	60	0	0	0	0	60
TOTAL	7819	12708	9797	1892	3565	14856	50637

Source: PEDCO Bimonthly Report entitled, "The Status of Flue Gas Desulfurization Systems in the United States", April-May 1977.

Two regenerable FGD systems (that produce a marketable sulfur or sulfuric acid by-product) were currently in operation at the demonstration level. Magnesium oxide scrubbing was in use at Philadelphia Electric's Eddystone No. 1 facility, and the Wellman-Lord/Allied Chemical Sodium Sulfite scrubbing process was demonstrated at Northern Indiana Public Service Company's Mitchell No. 11 plant and at Public Service Company of New Mexico's San Juan facilities.

Although approximately 51,000 MW of scrubbing capacity were operational, under construction, or planned for installation, controversy still existed on several key issues concerning the utilization of FGD systems. Several of these, including reliability, cost, secondary pollutants, and the ability of vendors to meet expected FGD market demands, are discussed in the following sections.

4.4.1 FGD Reliability

Scrubber opponents argue that U.S. experience with scrubbers has been disastrous. Unreliable systems such as Commonwealth Edison's Will County Station, Duquesne Light's Phillips Station, Kansas City P&L's Hawthorne Station, and Kansas P&L's Lawrence No. 4 station are often cited. In addition, the scrubber at Union Electric's Meramec Station, which was the basis for the SO_2 NSPS for steam generators, has been abandoned. Opponents also claim that FGD systems jeopardize power plant reliability, leading to the possibility of brownouts and blackouts due to forced power plant outages.

Scrubber proponents admit reliability problems with the early units; however, they cite substantially improved operations since the initial facilities were installed. Commercial facilities which have demonstrated high (70-90% or greater) reliability over extended periods of time include: Arizona Public Service's Cholla Station, Kansas City P&L's LaCygne Station, Kentucky Utilities Green River Station, Louisville Gas and Electric's Paddy's Run No. 6 Unit, Northern States Power's Sherburne Station and Pennsylvania Power's Bruce Mansfield Station. These units include both lime and limestone systems on low- and high-sulfur coals with unit sizes ranging from 65 MW at Paddy's Run to the 835 MW Bruce Mansfield Unit, which is the largest scrubbing unit in the world.

Although there has been a discernible improvement in reliability for FGD facilities installed in recent years, it is risky to flatly predict trouble-free operation for future installations since each application involves different fuels, process flow sheets, and operator and vendor capabilities.

Objective analysis would seem to indicate that there have indeed been problems with FGD reliability, and certainly, any equipment added to a power plant will have a tendency to reduce overall reliability. The reliability of scrubbers seems to be improving as the technology develops. There is, nevertheless, a continuing debate about the effect that FGD will have on power plant operations. Definitive answers to these questions will require more operating time on existing FGD units and the construction of new units that represent state-of-the-art improvements in FGD technology.

4.4.2 FGD Costs

A second major issue associated with FGD technology is that of cost and the relative trade-offs of cost versus environmental impact. Scrubber opponents argue that scrubbers are prohibitively expensive, requiring a large fraction of utility industry investment capital and substantially increasing the cost of electricity to the user. They claim that scrubber investment costs are not reasonable in light of the minimal environmental benefits to be gained. Scrubber proponents feel that the health and ecological impacts of SO_2 emissions are significant and that scrubber costs are not prohibitive in view of these impacts. The following discussion is intended to provide the reader with a rough idea of FGD costs (as of June 1977). A more exacting analysis can be found in the Process/Subsystem Summary Papers in Appendix B.

The ultimate cost of commercial-scale FGD systems varies widely depending upon such factors as the fuel sulfur content, type of absorbent, size of the installation, new versus retrofit unit, degree of SO_2 removal, energy and raw material requirements, and system complexity. Published costs range from unrealistically low to ridiculously high. The most comprehensive and detailed cost study to date is the TVA five process study published in November 1974 (MC-147). FGD capital costs were determined in this study to be between \$40 and \$80/kW for typical coal-fired applications. Corresponding annualized costs were 2.5 to 5.0 mills/kWh. Because of escalation in equipment and construction costs, an adjustment of 25-30% is required to bring these costs up to 1977 dollars. Realistically, FGD capital costs for large-scale (500-1000 MW) electrical generation plants should range from \$60 to \$150/kW with annualized costs of 3.0 to 6.0 mills/kWh. The annualized cost of FGD usage on a commercial basis is approximately 0.28 to 0.56 mils per million joules (30 to 60 cents per million Btu) of fuel consumed. An important issue related to FGD costs is that of parisitic energy usage, The "energy penalty" associated with FGD system operation. Current studies indicate that total energy supplied to the boiler must be increased by some 3-7% depending on FGD type, coal type, and other parameters.

4.4.3 Secondary Pollutants

A third issue in FGD technology development is that of secondary pollution from the FGD unit. The major issue here has been the large quantities of waste material (sludge) produced by nonregenerable FGD processes. A comprehensive research and development program, under EPA sponsorship, is currently under way to characterize FGD sludges and to develop and assess disposal and utilization methods. Based on available information, the best methods currently available for sludge disposal are landfilling of chemically-fixed sludge or disposal of untreated sludge in ponds lined with an impervious material such as clay, plastic, or rubber. Alternate methods, including mine and ocean disposal, are currently under study. Another major alternative is FGD sludge utilization. For example, there are expected to be limited markets in the wallboard and Portland cement industries for gypsum produced from FGD sludge. Technology also exists for the utilization of scrubber sludge in products such as bricks, road base materials, artificial aggregate, and aerated concrete. Other uses for FGD sludge, for example as a filler material in fertilizers, are currently being studied. However, because of uncertainties in marketing FGD byproducts, most of the FGD sludge produced, at least in the short term, will probably be discarded. For this reason, and because disposal presents a greater potential for adverse environmental effects than utilization, the major thrust of the EPA sludge program has been concerned with it. Sludge disposal thus remains a major problem in FGD application that will have to be resolved by RD&D efforts.

Recent evidence indicating the potentially harmful effects of sulfate species in the atmosphere has focused attention on FGD systems as potential emitters of sulfates. While there is the possibility of direct emission of small amounts of sulfates from FGD systems, the essential question concerns the potential for subsequent atmospheric conversion of the emitted SO_2 to sulfates. An uncontrolled source emits nearly all of the sulfuric acid mist and SO_2 formed in the boiler. However, an FGD system will remove greater than 50% of the sulfuric acid mist and 90% of the SO_2 which would be emitted to the atmosphere from an uncontrolled source. Thus, actual and potential sulfate emissions from a controlled source are significantly reduced (ST-537).

4.4.4 Ability of Vendors to Meet Expected Market Demands

In view of the relative lack of maturity of FGD technology, a major issue is the ability of the FGD vendors to meet demand for FGD systems. As discussed earlier and presented in Table 4-2, it is possible to meet the coal use goals in the NEP and still effect a net 3 percent reduction in SO emissions over those forecast for 1985. To accomplish this level of control, a total FGD capacity of 143,000 MW will be required by 1985 as shown in Table 4-5. This assumes that low sulfur coal without scrubbing will not provide the degree of control necessary and that advanced technologies (e.g., fluidized bed combustion, coal gasification, etc.) will not have a significant impact by 1985.

TABLE 4-5. PROJECTED SCRUBBER DEMAND (MW)
(Source: US-768)

	Base Case 1985	President's Program 1985	Increase
Utility	52,900	83,200	30,300
Industrial	8,900	60,600	51,700
Total	61,800	143,800	82,000

As of June 1977, there were 20,500 MW of scrubbing capacity either operational or under construction in the U.S. (see Table 4-4). This means that under the NEP, an additional 123,000 MW of scrubber capacity must be built before 1985. The vendor's ability to respond to widespread demands for FGD systems resulting from the mandated expansion in coal combustion has been questioned.

However, in a study by the International Gas Cleaning Institute, scrubber manufacturers were asked to assess the industry's ability to meet future demand (IN-139). The manufacturers estimated that with existing staff, 81,000 MW of scrubber capacity could be installed between 1978 and 1985. Under conditions of high market demand, the manufacturers estimated that 144,000 MW of capacity could be installed in the same time frame. It should be noted that three of the leading manufacturers, Combustion Engineering, CEA, and American Air Filter, did not respond to this survey. Thus, assuming this survey adequately reflects the industry's ability to respond quickly to changes in the marketplace, projected scrubber demand under the NEP in 1985 could be met.

4.5 Present Status of Alternative Controls for SO_2 Emissions

The coal-based technologies that have been considered as alternatives to conventional boilers equipped with FGD systems include: 1) the use of low sulfur coal, 2) the use of physically or chemically cleaned coals, 3) the use of fuels derived from chemical processing of coals, i.e., coal which has been processed for sulfur removal or to produce low sulfur gaseous or liquid fuels, and 4) advanced combustion systems such as fluid bed combustion. Table 4-6 illustrates projected costs and development times for each of these technologies. Since many of these technologies are not yet commercial, the cost data presented are only estimates, and there is some controversy as to the relative costs of these alternative SO_2 emission control strategies.

TABLE 4-6. PROJECTED COMMERCIALIZATION DATES AND BUSSBAR POWER COSTS FOR ALTERNATE SO_2 CONTROL TECHNOLOGY

Technology	Projected Commercialization	Bussbar Power Costs (Mills/kWh)
Low Sulfur Coal	Current	28
Atmospheric Fluidized Bed Combustion	1984-1986	30
Lime FGD	Current	35
Pressurized Fluidized Bed Combustion	1986-1988	36
Chemical Coal Cleaning	1983-1985	36
Coal Liquefaction	1983-1985	43
Low-Btu Coal Gasification	1980-1982	49

Source: BA-596, PO-177

It has been established that only about 9% of this country's coal reserves are low enough in sulfur to meet present NSPS's (PE-289). In addition, the recent Clean Air Act Amendments may prohibit the use of low sulfur coal alone to achieve compliance with SO_2 regulations.

Physical coal cleaning can be adapted to remove up to 80% of coal pyrites (comprising 20 to 80% of total sulfur content depending upon the characteristics of the coal) but, to accomplish this, more refined processing methods are necessary. None of the plants currently in operation produce coal capable of meeting Federal SO_2 regulations. Chemical coal cleaning has the potential for removing 95% of the pyritic sulfur and 40% of the organic sulfur. EPA is currently conducting tests on a prototype unit using an aqueous ferric sulfate leaching process and is also evaluating seven or eight other processes for future study. However, commercialization of chemical coal cleaning processes is not expected before the mid-1980's.

Coal gasification and liquefaction processes which are under development will have the capability of producing low sulfur fuels. Based upon current estimates, it appears that these technologies may not be economically competitive with FGD in base load power generation There is uncertainty associated with this analysis, however, because of the impact of future regulations. In addition, economics for these processes may improve if highly efficient high temperature gas turbine/steam combined cycles are developed. Such combined cycle systems are currently believed to be at least ten to fifteen years away from commercialization.

In any event, commercialization of competing coal conversion technologies is not expected before 1985 and FGD thus appears to be the most viable alternative for SO_2 emission control until then. There is also a significant chance that FGD will continue to be the most competitive alternative after 1985. Consequently, the potential for SO_2 emission control by conversion of coal to a liquid or gas does not seem to adversely impact the desirability of further development of FGD.

Of the advanced direct coal combustion systems which have been considered for utilization of coal in an environmentally sound manner, only fluid bed combustion (FBC) appears to have potential for commercialization in the relatively near term. Some studies have shown a significant (10%) cost savings of atmospheric FBC over scrubbers. Historically, however, costs have escalated for technologies evolving from pilot to commercial scale. Also, although the first commercial FBC units are expected to be installed in the 1980's, significant impact on overall coal consumption will not come until after 1985. Consequently, FGD appears to be the primary technology for SO_2 control capable of widespread application before 1985, and there is a significant chance that it will continue to be competitive with FBC after that time.

4.6 Current and Planned FGD RD&D Programs

A brief summary of the major FGD programs currently underway or planned by U.S. organizations is presented in this section. This summary includes participants, objectives, status, and scale for each of the current or planned programs. These programs were used in this study as the basis for evaluating potential new programs to determine what benefits could be obtained from further research.

In the last decade, research into methods of removing SO_2 from stack gas has intensified. The main impetus in this direction has come from government agencies in the U.S., Japan, and West Germany. The major programs, both current and planned, of four U.S. groups in the forefront of FGD research (The U.S. Environmental Protection Agency, Electric Power Research Institute, Tennessee Valley Authority, and the Bureau of Mines) are summarized in Table 4-7 and described later in this section. These programs represent most of the current U.S. RD&D activity.

In addition to these organizations, the Department of Energy maintains a continuing program to evaluate the impact of FGD technology on energy programs and is also sponsoring an evaluation of the Sulf-X Process.

While it is possible that some FGD technology will be imported directly from Japan, most of the advances in FGD technology will probably come from these five organizations working in concert with U.S. and foreign industrial groups. At present, substantial RD&D capability exists which is needed to accelerate the commercialization of FGD technology. It is clear, however, that funds likely to be available will not permit undertaking all potentially useful programs. A summary of the current and planned FGD RD&D programs listed on Table 4-7 is presented below.

4.6.1 Lime/Limestone Programs

EPA Pilot FGD Scrubber Program - Located at IERL-RTP, two 0.1 MW capacity scrubbers have been in operation since 1972. These facilities have been the basis for many of the RD&D programs later carried out at larger scales. They provided excellent in-house support for the work at Shawnee as well as a location to evaluate new concepts independent of the Shawnee work. The data obtained from these 0.1 MW plants, along with Shawnee data, have been used to develop models for predicting SO_2 removal as a function of parameters such as L/G, SO_2 concentration, pH, magnesium concentration, and pressure drop.

Shawnee Steam Plant - (EPA/TVA) - The test facility at the Shawnee Steam Plant is a flexible system which allows testing of up to three 10 MW scrubber types under a variety of operating conditions. RD&D completed or planned includes a) characterization of the effect of process variables on SO_2 removal, b) development of a design/economic study computer program, c) optimization of the process with regard to costs, energy requirements, and quantity and quality of sludge (including forced oxidation), d) improvement of system control and reliability, e) evaluation of various mist elimination techniques, f) investigation of process improvements using additives such as MgO, and g) investigation of subsaturated gypsum operation. The Shawnee test facility

TABLE 4-7. MAJOR CURRENT[1]/PLANNED PROGRAMS OF AGENCIES INVOLVED IN FGD RD&D

Environmental Protection Agency (EPA)

- IERL-RTP lime/limestone in-house pilot plant, 0.1 MW
- Advanced testing lime/limestone at Shawnee, 10 MW
- Wellman-Lord demonstration, 115 MW
- R.I. Aqueous Carbonate Process demonstration, 100 MW
- Citrate demonstration, 60 MW with Bureau of Mines
- Bahco Program - lime scrubbing
- LG&E Test Program - subsaturated gypsum operation, 65 MW
- Colbert Steam Plant Program - 1 MW pilot plant
- Double Alkali prototype, Scholtz Station, 20 MW
- Double Alkali demonstration, 280 MW
- Support Studies - economics, reductant gases, by-product marketing

Electric Power Research Institute (EPRI)

- Testing of Chiyoda 101, Bergbau-Forschung, Double Alkali at Scholtz, 20 MW
- Testing of Chiyoda 121 at Scholtz, 20 MW
- Resox demonstration in Lünen, Germany, 42 MW
- Testing of R.I. ACP as support for EPA demonstration, 5 MW
- Colbert Power Plant - reheat, corrosion/erosion, cocurrent scrubbing, sludge characterization, 1 MW
- Evaluation of improved process control capability
- Dowa prototype - 10 MW at Shawnee

Tennessee Valley Authority (TVA)

- Advanced testing of 10 MW lime/limestone at Shawnee
- Colbert Power Plant facility with EPRI, 1 MW
- Dowa prototype - at Shawnee, 10 MW
- Colbert Steam Plant Program with EPA, 1 MW pilot

Bureau of Mines (BOM)

- Citrate Demonstration, 60 MW with EPA

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[1] Late 1977

has proven flexible enough to evaluate many process problem areas and innovations prior to demonstration at the 100-200 MW level.

Shawnee 10 MW Testing - (EPRI) - In 1978 EPRI will begin testing improved FGD design concepts at Shawnee. The project is directed at designing and constructing a 10 MW co-current/countercurrent spray scrubber. In addition, consideration is being given to modifying the TCA scrubber system to operate in a limestone regenerable double alkali mode (DOWA scrubbing system).

Bahco Program - (EPA) - The Air Force installed an AB Bahco Ventilation (Sweden) lime scrubbing process on seven small coal-fired boilers (21 MW capacity total) at Rickenbacher Air Force Base. The Bahco system appears particularly well suited for small industrial applications and is manufactured in 5-50 MW equivalent sizes. EPA has recently completed a 2-year test program on this system. Although acceptance tests have not yet been completed, SO_2 removal efficiencies have consistently exceeded design specifications.

LG&E Scrubber Test Program - (EPA) - In November 1974, pilot unit testing at IERL-RTP indicated that lime and limestone scrubbers could be operated subsaturated with gypsum to avoid scaling of scrubber internal surfaces. The scrubber at LG&E's Paddy's Run Station was found to operate in this mode. A program was initiated in 1976 to evaluate operational and chemical factors identified by IERL-RTP pilot unit work which seemed to affect subsaturated operation. There were four phases of testing: a) carbide lime testing (normal operation), b) commercial lime testing, c) reaction tank modification testing, d) MgO/Cl addition testing. The data from this testing are currently being evaluated.

Development of Improved Lime/Limestone Scrubbing Technology - (EPRI-TVA) - This 18-month project is an expansion of an existing development and process evaluation program at the TVA Colbert pilot plant (1 MW). Testing has been completed on a 1 MW horizontal scrubber and a 1 MW cocurrent scrubber. Evaluations will also consider scrubber effects on reheat, corrosion/erosion, and mist elimination.

Evaluation of Improved Process Control Capability - (EPRI) - This two year study will evaluate the state-of-the-art performance, reliability, and cost data on process control subsystems on existing lime/limestone scrubber installations.

4.6.2 Double Alkali Programs

CEA-ADL Program[1] - (EPA/EPRI) - After successful bench and pilot scale facilities were built and operated by ADL, the project was expanded to include a prototype test at the 20 MW facility at the Scholtz Steam Plant. The testing of this system was completed in July 1976. On the whole, the prototype performed well and indicated that a double alkali system could be a viable FGD process for coal-fired facilities. SO_2 removal was generally between 90-99%. The next step in the development is a demonstration-size facility.

LG&E Double-Alkali Demonstration - (EPA) - EPA contracted with LG&E in 1976 for a full-scale demonstration of the double-alkali process at the 280 MW Cane Run No. 6 boiler (coal-fired). The four phases of the project are: a) design and cost estimation, b) engineering design and construction, c) start-up and performance testing (early 1979 expected), and d) one year operation and optimization.

4.6.3 Regenerable Processes

Magnesia Slurry Program - (EPA/EPRI) - In 1974 EPA and Boston Electric completed a demonstration program of a 155 MW magnesium oxide process. Two years of operation proved that >90% SO_2 removal was possible and that high quality acid could be produced. However, continuous long-term, reliable operation was not achieved.

EPA and Potomac Electric jointly participated in a 100 MW demonstration in 1973. Greater than 90% SO_2 removal was achieved and high quality acid was produced. Due to a shortage of funds and time the program was not able to answer all questions concerning absorbent recycle and losses, or operating reliability.

Philadelphia Electric will soon begin operating a 120 MW MgO system. This facility, like the other two, will produce acid.

Wellman-Lord Demonstration - (EPA) - EPA and NIPSCO (Northern Indiana Public Service Co.) have cofunded the design and construction of a Wellman-Lord scrubbing system which has been retrofitted to the 115 MW, coal-fired unit 11 at the D.H. Mitchell Station. The Allied Chemical SO_2 reduction process is being used to convert SO_2 to elemental sulfur.

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[1] Combustion Engineering Associates - Arthur D. Little

Aqueous Carbonate Demonstration - (EPA) - EPA, EPRI, DOE, and Empire State Electric Energy Research Corporation are cofunding the design and construction of an International Aqueous Carbonate Process demonstration. This sulfur-producing process is being retrofit to Niagara Mohawk Power Company's 100 MW coal-fired Huntley Station. The program is scheduled to be completed by late 1980 and will include complete performance and optimization testing of the system.

BOM Citrate Demonstration - (BOM/EPA) - St. Joe Minerals Corporation, the U.S. Bureau of Mines (BOM) and the EPA are jointly sponsoring a 60 MW demonstration of the BOM Citrate Process, retrofit to a coal-fired boiler at St. Joe Minerals' zinc smelter in Monaca, Pennsylvania. This demonstration will produce elemental sulfur from the recovered SO_2. The project is scheduled to be completed in late 1980 and will include complete performance and optimization testing of the system.

Catalytic Oxidation Demonstration - (EPA) - EPA and Illinois Power Company attempted to demonstrate the reheat Cat-Ox Process on a 103 MW coal-fired boiler at the Wood River Station beginning in 1970. The unit passed all performance guarantees and was accepted in mid-1973. However, numerous problems subsequently precluded successful operation of the plant. A detailed technical and economic study of the situation resulted in the termination of the project in December 1976 prior to optimization testing and long-term reliability testing.

Scholtz Steam Plant Studies - (EPRI) - The Southern Company installed 20 MW plants of three FGD systems at the Gulf Power Scholtz Plant. The process evaluated were: a) ADL/CEA Double Alkali, b) the Foster Wheeler/Bergbau-Forschung Process, and c) the Chiyoda 101 Dilute Acid Process. The testing of the Chiyoda 101 Process was not completed and the remaining funds for this phase were used for a test of the Chiyoda 121 Process.

Resox Demonstration - (EPRI) - EPRI is funding the design, construction, and operation of a 42 MW Resox unit in Lünen, West Germany. This plant is applied to an operating Bergbau-Forschung unit and has gas blending facilities that can simulate alternative process "front-end" feeds of SO_2. Objectives are to: a) prove long-term reliability, b) confirm Resox designs, c) demonstrate flexibility by processing SO_2 streams which have been simulated to duplicate Wellman-Lord MgO, and absorption-steam stripping SO_2-rich streams, and d) demonstrate load-following capability.

Aqueous Carbonate FGD Process Development - (EPRI) - This project supports the EPA-ESEERO Aqueous Carbonate Process (ACP) demonstration plant. The tests will be performed at RI's 5 MW facility in Canoga Park, California. Key questions to be addressed are the system's ability to handle coal, and the tapping, quenching, and dissolution of a salt/ash melt. Work should be completed by mid-1978.

Absorption/Steam Stripping - (EPRI) - EPRI has funded a bench-scale program to evaluate the feasibility of sorption/steam stripping as an FGD system. The equipment is designed to test absorption characteristics and the energy requirements of regeneration for a variety of sorbents.

4.6.4 Support Studies for FGD Systems

Reductant Gases - (EPA) - EPA has completed an initial study of the technical and economic feasibility of using low-Btu gas produced from coal as a reductant in FGD systems. The study concludes that use of a gasifier would significantly increase the complexity of an FGD system; however, the gasifier could be used to supply some process energy requirements such as stack gas reheat.

By-Product Marketing Studies - (TVA) - TVA has developed a computer program to identify optimum production and distribution patterns of sulfur, sulfuric acid, and gypsum as a function of SO_2 removal regulations.

Comparative Economics of SO_2 Control Processes - (EPA/TVA) - This is a continuing effort to evaluate the most promising FGD systems with regard to their relative economics. Processes evaluated include Lime/Limestone, Double Alkali, Citrate, Magnesia Slurry, Wellman-Lord, and Cat-Ox.

Engineering Applications/Information Transfer - (EPA) - This program disseminates FGD technological data and information to the user community. Materials being prepared as part of this program include: 1) summary reports on well-developed FGD technologies, 2) a series of quarterly reports on FGD research, development, and demonstration efforts, and 3) lime and limestone scrubbing data books. These materials will augment EPA's existing program of symposiums, reports, and personal communications to assure the efficient and effective dissemination of information on pollution control technology.

5.0 IDENTIFICATION AND EVALUATION OF FGD RD&D NEEDS

The need for additional RD&D to resolve questions of operating reliability, cost, energy requirements, and secondary pollution for existing FGD technology was addressed in Section 4. This section describes the evaluations undertaken to arrive at specific RD&D recommendations that would either enhance current or developing technologies, or that would offer new and improved approaches to FGD.

5.1 Ground Rules and Assumptions

The following ground rules and assumptions were made:

1) The study would be completed in six months to allow impact on EPA's FY78 and FY79 program plans.

2) There would be extensive coordination and review within the Federal government to provide the broadest possible perspective for the study.

3) Both processes and subsystems were to be evaluated. (Processes are defined as complete FGD systems, while subsystems are those parts of FGD processes that can be used almost interchangeably in several FGD processes.) By evaluating subsystems, it should be possible to identify improvements to existing and developing processes as well as to entirely new processes.

4) Processes and subsystems evaluated must be capable of being commercialized in time to be competitive with alternate technologies (by 1985).

5) Processes and subsystems selected for detailed evaluation must show economic, environmental, or technological advantages over existing or developing FGD systems.

6) Processes and subsystems which have demonstrated or have capability for NO_x or fine particulate removal would be given special consideration.

5.2 Organization and Methodology

The objectives of this study were to:

- Review existing and proposed FGD programs to identify the need for additional RD&D to accelerate the commercialization and acceptance of FGD systems.
- Identify the specific RD&D programs that should receive funding.
- Estimate the level of funding necessary to implement the RD&D projects recommended.

To assure the widest possible perspective, several different government agencies were invited to participate in this study. It was to be administered by EPA, and use contractors to provide the necessary technical input. Review was solicited from knowledgeable private individuals and organizations. The task which faced EPA was that of developing a methodology which would allow the program objectives to be met in the limited time available and still provide for the broadest possible input. The program organization and the methodology developed are briefly discussed below.

5.2.1 Organization

The overall study was chaired by George R. Hall of the Executive Office of the President, Office of Energy Policy and Planning (OEPP). The study utilized three groups: the Technical Working Group, the Interagency Steering Panel, and the Liaison Group. The function and makeup of each of these groups is described below:

Technical Working Group

This group was chaired by Dr. Stephen J. Gage, Assistant Administrator for Research and Development, EPA. Other members of the group were Lewis Faucett (TVA), Stuart Dalton (EPRI), Myron Gottlieb (DOE), Lawrence H. Weiss (Chem Systems), A.V. Slack and Milton R. Beychok (independent consultants). The functions of the Technical Working Group were to:

1) Assist in developing screening criteria to be applied to a comprehensive list of FGD processes/subsystems.

2) Review the initial screening results,

3) Assist in developing evaluation criteria to be applied to the processes/subsystems selected for detailed evaluation,

4) Conduct the detailed evaluation of candidate processes/subsystems,

5) Assess the schedule and costs of the process/subsystem RD&D options,

6) Make recommendations regarding RD&D opportunities, and

7) Review the draft final report.

Interagency Steering Panel

The Interagency Steering Panel provided overall guidance in approach and methodology, reviewed study products with emphasis on the final report, and approved the study conclusions and recommendations. Members of the Interagency Steering Panel were Samuel Biondo (DOE), Bernard Chew (DOE), Howard Feibus (DOE), Stephen J. Gage (EPA), S. William Gouse (DOE), G. R. Hall (DOE), Gerald Hollinden (TVA), David Israel (DOE), K. H. Jones (CEQ), Judy Kammins (OMB), Rafael Kasper (OST), Susan Hickey (FEA), Richard Hertzberg (OMB), C. Morgan Kinghorn (OMB), William E. Mott (DOE), Frank Princiotta (EPA), Jack Silvey (DOE), and Kenneth Woodcock (DOE).

Liaison Group

The Liaison Group provided input from other organizations which had interest in the study. Liaison with these organizations was necessary to obtain the broadest possible perspective for the study. Included in the group were R. W. Crozier (NAE), Lloyd Taylor (SAB), H. W. Elder (TVA), and Kurt Yeager (EPRI). Interface with the Liaison Group was handled by Richard D. Stern of EPA's Industrial Environmental Research Laboratory (IERL-RTP).

5.2.2 Methodology

The approach and schedule developed for completing the program objectives is shown schematically in Figure 5-1. Shortly after initiation of the study, EPA contractors, with the aid of consultants, developed an initial list of processes/subsystems and an initial set of evaluation criteria. EPA then set up a series of meetings with the Working Group, the contractors, the Steering Panel, and the Liaison Group to review and comment on the initial process/subsystem list and initial screening criteria.

A total of 138 processes were surveyed (by the preparation of an Information Survey Paper for each) and then screened as to their potential for offering technological and/or economic advantages over the following six commercial and developing FGD processes:

- Lime/Limestone Wet Scrubbing
- Magnesia Slurry Scrubbing
- Wellman-Lord
- Sodium/Lime Double Alkali
- Citrate Buffered Absorption
- Rockwell International - Aqueous Carbonate Process

At this time, a public meeting was held in Washington to acquaint the public with the scope and objective of the study, to solicit additional information for the study, and to request comments on EPA programs. As a result of this study, two processes were added to the comprehensive list for evaluation.

Results of the screening indicated that 13 new processes/subsystems should be evaluated in detail along with these six processes. Next, Process/Subsystem Summary Papers were prepared for each of these 19 processes/subsystems. The detailed evaluation criteria developed by all groups were applied to each process/subsystem by the Technical Working Group. The Liaison Group and the Working Group then provided EPA with a list of recommendations for RD&D based on the evaluations, and a draft report was prepared. This draft was reviewed by all three groups, and suggested revisions were incorporated in the final report. A detailed discussion of each of the steps outlined here and on Figure 5-1 is given in the following two sections. The methodology and the results of the initial screening are presented in Section 5.3. The detailed evaluations are presented in Section 5.4.

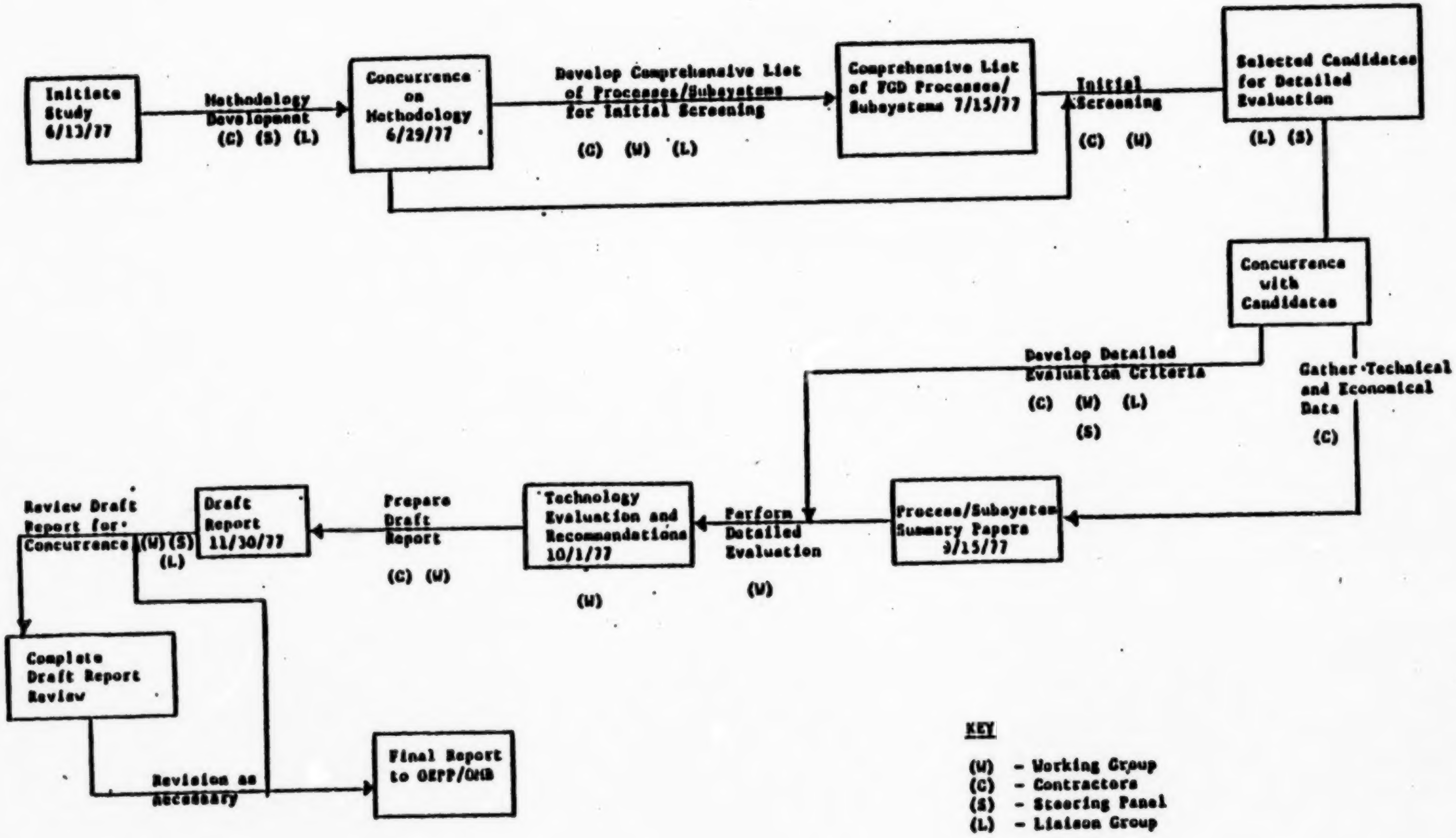
Initiate Study 6/13/77
Methodology Development
(C) (S) (L)
Concurrence on Methodology 6/29/77
Develop Comprehensive List of Processes/Subsystems for Initial Screening
(C) (W) (L)
Comprehensive List of FGD Processes/Subsystems 7/15/77
Initial Screening
(C) (W)
Selected Candidates for Detailed Evaluation
(L) (S)
Concurrence with Candidates
Develop Detailed Evaluation Criteria
(C) (W) (L)
(S)
Gather Technical and Economical Data
(C)
Process/Subsystem Summary Papers 9/15/77
Perform Detailed Evaluation
(W)
Technology Evaluation and Recommendations 10/1/77
(W)
Prepare Draft Report
(C) (W)
Draft Report 11/30/77
Review Draft Report for Concurrence (W) (S) (L)
Complete Draft Report Review
Revision as necessary
Final Report to OEPP/OMB
KEY
(W) - Working Group
(C) - Contractors
(S) - Steering Panel
(L) - Liaison Group

Figure 5-1. Interagency FGD technology evaluation study approach and methodology.

5.3 Selection of Candidate Processes/Subsystems*

In order to select candidate processes/subsystems, the following tasks were performed:

- A comprehensive list of processes, subsystems, and alternatives was prepared.
- A set of evaluation criteria to aid in screening the processes was developed.
- Information on each process was gathered and compiled in the form of a brief Information Survey Paper.

Each of these tasks is discussed in more detail in the following sections.

5.3.1 Comprehensive List of Processes

The initial step in the candidate process selection was to develop a comprehensive list of FGD processes and subsystems. Two contractors, Radian Corporation and TRW, were retained to aid in this effort.

An initial process list was prepared by performing an exhaustive literature search and combining the files of EPA, EPRI, TVA, and the two contractors. International FGD developments, predominantly in Japan and Germany, were included in the list. This list was then reviewed by the Technical Working Group, and several additional processes were added. In addition, a public meeting was held to solicit public input. The final list consisted of some 138 processes and subsystems which are presented in Table 5-1.

5.3.2 Criteria for Candidate Selection

Evaluation criteria were established to provide an objective and consistent means of comparing the processes and to insure that the same factors were considered for each process. The criteria were applied by assigning numerical ratings to each process, based on qualitative judgments about its merits. Although the criteria developed could not be detailed enough to allow for all of the various advantages and disadvantages of the processes, they were a useful beginning for the process screening. The major criteria used for the evaluation are described

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*Both processes and subsystems were considered in this candidate screening. However, they will be referred to henceforth as "processes" in the discussion.

TABLE 5-1. COMPREHENSIVE LIST OF POTENTIAL CANDIDATES FOR DETAILED EVALUATION

Throwaway Systems	Regenerable Systems	Subsystems	Others
Agglomerating Cone Alkaline Ash Scrubbing Ammonia Scrubbing/H_2SO_4 Acidulation (Cominco, Amnox) Ammonia Solution Double Alkali Ammonia Vapor Double Alkali (Ugine Kuhlman, Nippon Kokan) ClO_2 Calsox Carbon Adsorption (Hitachi, Lurgi-Sulfacid) Chisso Engineering Chiyoda Thoroughbred 101 Chiyoda Thoroughbred 102 Chiyoda Thoroughbred 121 Double Alkali with Limestone (Showa-Denko, Kureha-Kawasaki) Dowa Aluminum Sulfate Dry Alkalis plus Fabric Filter Ebara-Jaeri Holter Ishikawajima-Harima HI IPRAN Kawasaki MgO/Lime Koyo Krebbs-Neville Kurabo Kureha (SO_2/NO_x) Kureha Sodium Acetate Lead-Zinc Ore Lewis Process Micropul Mitsubishi Heavy Industries Moretana Calcium Moretana Sodium Red Mud RIIC SCRA Sea Water Simon Carves Sodium Carbonate Scrubbing Sodium Hypochlorite Sulfurtain	WET Ammonia Bisulfate (ABS) Ammonia Evaporative Crystallization Ammonia/IFP (Catalytic, Research Cottrell) Aquaclaus ASARCO Dimethylaniline Consol Grillo ICI Steam Stripping Johnstone Zinc Oxide Luri Sodium Aluminate Magot McKee MeLamine Mitsui Eng. & Shipbuilding Molten Carbonate Molten Potassium Carbonate/Thiocynate NIIOGAZ Ammonia/Steam Stripping NIIOGAZ Magnesium Oxide NOSOX Peabody Potassium Bisulfite Potassium Formate Potassium Sulfite Ralph Parsons Spring-Nobel Hoechst Stone & Webster/Ionics Sulf-X TSK Sulfix UOP Sulfoxel DRY Alkalized Alumina Bergbau-Forschung Bureau of Mines MnO_2 Carbon Adsorption/Inert Gas Stripping (Reinluft/Chemiebau, Sumitomo) Copper Oxide Adsorption (Shell, Esso B&W, Bureau of Mines) Callery Chemical Hormel Houdry In-Situ CO Reduction (Chevron) In-Situ H_2S Reduction (Peter Spence, Princeton Chemical, Ontario Research Foundation) Integrated Cat-Ox Kiyoura-TIT Mitsubishi Manganese Oxide Purasiv S Rohm & Haas Resin Adsorption Shuffman Sumitomo Heavy Industries TOPSOE Tyco Chamber Unitika Uranium Oxide Westvaco	Allied Reduction Process ASARCO Sulfur Plant Calcium Sulfate Regeneration Citrate Double Loop Regeneration Claus Process Concurrent Scrubbing Dilute System Sulfate Removal Direct Production of Sulfur from $MgSO_3$ Forced Oxidation of $CaSO_3$ IFP Subsystems Ionics Electrolytic Regeneration Mass Transfer Additives with Lime/Limestone Scrubbing Production of Reducing Gas RESOX Sludge Stabilization Tampella Recovery Process	Allied Chemical Electrodialysis Allied Chemical Membrane Process Barium Carbonate Battelle Fused Salt Boliden Catalox Cooper Condensation and Reaction with Fly Ash Dry Removal with Ground Lime Dry Sorbents Electrochemical Concentration Esso (V_2O_3) Goodrich ITT McCauley MgO Based Double Alkali Reduction with "Blue Gas" Siemens Soil Process Sulfuric and Nitric Acid Recovery Method

briefly below and are presented in more detail in Appendix A.

1) Minimum Requirements - These criteria provided a preliminary screening to eliminate processes that would not comply with the ground rules of the study from further consideration.

    - A process/subsystem must be able to achieve compliance with an assumed future NSPS for SO_2. In this study, if a system could not reduce SO_2 emissions to 0.4 lb $SO_2/10^6$ Btu when firing low sulfur Western coal, it was eliminated from consideration because development of such processes would not be of sufficient long-term benefit.

    - A process/subsystem must be able to treat flue gases resulting from coal combustion.

    - Adequate information must be available to allow process/subsystem evaluation.

2) Environmental and Energy Considerations - These criteria examined such factors as SO_2 removal, multipollutant removal, secondary pollutant problems, raw material requirements, potential for overall performance growth, and relative energy requirements. Consideration of process/subsystem energy requirements involved the following questions.

    - Does the process require reheat?

    - Is reducing gas required?

    - Are the absorber/adsorber L/G or ΔP requirements expected to be relatively low, medium, or high?

    - Are other energy requirements expected to be relatively low, medium, or high?

3) Development Status - These criteria examined the relative amount of RD&D effort required to bring a process to commercialization. Included in these criteria were such factors as stage of development, degree of integration demonstrated, use of current technology, and anticipated scale-up problems.

4) Economic and Technological Considerations - These criteria examined the chemical and mechanical complexity of the various processes, thus providing a means of comparing anticipated process costs. This approach to comparing costs was used because of uncertainties in the economic data that were available. The general lack of economic data was due to the early development status of many of the processes being considered.

5) Applicability - These criteria examined the relative process applicability for both utility and industrial boilers and included factors such as ease of retrofit, decoupling ability, and by-product marketability. In addition, turndown ability was examined for utility applications, and the suitability of the process for modularization was examined for industrial application.

5.3.3 Information Survey Paper Preparation

Before the evaluation criteria could be applied to the comprehensive process list, information on each process had to be gathered and compiled into brief Information Survey Papers (ISP). The ISP's presented an engineering analysis of each process, permitting direct application of the evaluation criteria. Information necessary to prepare the ISP's came from the literature and from contacts with consultants and process developers. Following the engineering analysis, the evaluation criteria were applied using the information in the ISP's, and a "Summary and Conclusions" section was written for each process. This section presented the relative process ranking, its advantages and disadvantages, and a judgment as to whether the process should be considered for further evaluation. Copies of the ISP's for each process and subsystem, along with a list of references, are included in Appendix B.

5.3.4 Process/Subsystem Screening

The comprehensive list of processes was grouped into four categories: throwaway processes, wet regenerable processes, dry regenerable processes, and subsystems. Throwaway processes are those processes where sorbents are not regenerated or that produce a by-product with, at best, extremely limited marketability (sludge, gypsum, sodium sulfate, etc). Regenerable processes are those processes that can produce a potentially marketable by-product (sulfur or sulfuric acid). Subsystems are portions of FGD processes which may be used with other processes to improve their overall performance.

Process subsystems were categorized so that some processes from each group would be selected for further evaluation. This was desirable because each category of processes has unique inherent advantages and seems to be well suited for different applications and for different areas of the country.

In addition, a fifth process category entitled "others" was added. Processes included in this category possessed insufficient information to prepare ISP's, and thus the evaluation criteria could not be applied. The overall results of the process/subsystem screening were probably not significantly affected by the inability to evaluate these processes because, in most cases, development activities apparently ceased due to process technological or economic deficiencies.

The process evaluators felt that the evaluation criteria provided an effective means of comparing FGD processes. However, as is often the case when applying a generalized set of criteria to specific cases, some processes received high ratings even though they had limited acceptability due to some unique process characteristics. Also, some processes received low ratings due to their development status even though they were judged to have more potential than some of the processes with higher ratings. Therefore, engineering judgement was used along with the evaluation criteria. Processes which received high ratings but were not recommended for further consideration or processes which received low ratings but were recommended will be discussed in the following sections and in the process ISP's.

Screening of Throwaway Processes

A total of 45 throwaway processes were considered in the initial process screening. One did not comply with the minimum requirements for evaluation. The following processes offered potential advantages over commercial and developing FGD systems and were recommended for further evaluation based upon the information presented in ISP's, the evaluation of the process, and the judgment of the individual process evaluators.

Chiyoda Thoroughbred 121 - The CT-121 Process offers potential for significant cost reductions over conventional lime/limestone scrubbing. The use of a single vessel for scrubbing, forced oxidation, and precipitation could reduce both capital and operating costs. In addition, the gypsum product may have a lower potential environmental impact than the sludge from conventional lime/limestone scrubbers.

Dowa - The Dowa Process appears to offer potential benefits in the areas of environmental acceptability and cost compared to the sodium/lime double alkali systems. The process produces a gypsum by-product which is potentially more environmentally acceptable than the calcium sulfite sludge from sodium/lime double alkali systems. In addition, process operating costs should be lower since the process uses limestone rather than lime, as in other double alkali systems.

Hölter - The Hölter Process is claimed to have lower energy requirements than conventional lime/limestone systems due to reduced reheat requirements and lower liquid recirculation rates. In addition, process water requirements are lower, a clear solution is used for scrubbing, and the process produces a gypsum sludge which should have lower secondary pollution potential than sludge from conventional lime/limestone systems. The Holter Process thus offers potential improvements in system energy and raw material usage and in secondary environmental impacts.

Kurabo - The Kurabo Process appears to offer potential improvement over current technology in the areas of environmental acceptability, reliability, and SO_2 removal. The process can produce either gypsum, which is potentially more acceptable than calcium sulfite sludge, or ammonium sulfate which is potentially marketable as a fertilizer. The process operates in a dilute ammonia mode and is claimed to result in no ammonia sulfate fumes. The process appears to be less susceptible to scaling and to offer potential for high SO_2 removal at a lower cost than lime/limestone systems.

Sodium Based Throwaway System (Sodium Carbonate Throwaway, Dry Alkali with Fabric Filter, Koyo) - The sodium based (nahcolite, trona, Na_2CO_3, etc.) throwaway processes appear to offer significant potential as the least expensive FGD processes in those areas of the country where sodium is readily available. They have low energy requirements and are less complex than most competing systems. Thus, they appear to have potential advantages in the areas of cost and reliability.

The Chiyoda Thoroughbred 101 Process (CT-101) was not recommended for further evaluation even though it ranked high because it is being replaced by the Chiyoda Thoroughbred 121 Process. The sodium carbonate scrubbing process is examined in the paper on sodium based throwaway systems, which also presents two other sodium based processes (dry alkalis plus fabric filter and Koyo) as variations.

Several processes/subsystems which ranked high have the potential for enhancing or improving existing technologies. They are included as process alternatives in the Process/System Summary Papers on the existing technologies. The Double Alkali with Limestone Process is included as an alternative in the Process/Subsystem Summary Paper on the Sodium/Lime Double Alkali Process. The Kawasaki MgO/Lime Process is considered an alternative of the Lime/Limestone Process.

Several wet throwaway processes that remove both SO_2 and NO_x were considered in the screening. These processes are currently being developed in Japan. None of these processes were recommended for further consideration as part of this evaluation, due to the increased process complexity necessary for NO_x removal. In general, wet SO_2/NO_x removal systems do not compare well with systems designed solely for SO_2 because of the problems associated with absorbing NO_x from flue gases and the treatment of the resulting liquor. The benefit gained from NO_x removal does not appear to compensate for the added process complexity necessary for NO_x removal.

Screening of Wet Regenerable Processes

A total of 30 wet regenerable processes were considered in the initial process screening. Five did not comply with the minimum requirements for evaluation. Separate Process/Subsystem Summary Papers were prepared for the following processes which were felt by the evaluation panel to offer new or potentially improved approaches to FGD, based upon information in the ISP's, the evaluation of the processes, and the evaluator's engineering judgment.

Ammonia/IFP - The Ammonia/IFP Process appears to offer potential benefits in the areas of SO_2 removal and by-product disposal. The process appears capable of high SO_2 removal efficiencies and could be less costly than the current commercial processes. It also produces a marketable sulfur product as opposed to sludge, thus enhancing its environmental acceptability.

Melamine - The Melamine Process appears to offer potential advantages in SO_2 removal ability, relatively low secondary environmental impact and potentially lower energy requirements than other regenerable processes using a similar regeneration scheme, such as magnesia scrubbing. The process appears readily capable of greater than 99 percent SO_2 removal and could have significant advantages in such applications. The sulfuric acid produced should be marketable, and no sludge disposal is required. Also, energy consumption is potentially lower than in the magnesia slurry process.

Sulf-X - The process developers claim that the Sulf-X process is a relatively inexpensive process for simultaneous SO_x/NO_x removal. Although the process claims have apparently not been independently verified to date, the process' potential for multi-pollutant removal could offer advantages over other FGD processes. In addition, the process as presented produces sulfur directly, using coal as a reductant. Further investigation of vendor claims appears warranted.

In addition, the concept of sorption/steam stripping, which is used by many of the processes, offers potential advantages in terms of process simplicity and energy consumption. For this reason, a Process/Subsystem Summary Paper was prepared on the overall concept of sorption/steam stripping, including evaluations of the various sorption options. It also includes a number of processes in which SO_2 is sorbed in an aqueous or solid medium and then removed by steam stripping. The processes receiving high ratings which are included in the Sorption/Steam Stripping Process/Subsystem Summary Paper are NIIOGAZ Ammonia/Steam Stripping, ICI Steam Stripping, Peabody, NOSOX, and ASARCO Dimethylaniline.

Separate Process/Subsystem Summary Papers were not prepared for the Grillo and NIIOGAZ Magnesium Oxide Processes although they received the highest evaluations of wet regenerable processes. These processes are quite similar to the Magnesia Slurry Process and, therefore, were evaluated as process alternatives in the Magnesia Slurry Process/Subsystem Summary Paper.

Screening of Dry Regenerable Processes

A total of 27 dry regenerable processes were considered in the initial process screening. Five did not comply with the minimum requirements for evaluation. A significant feature of the dry process rankings was the low scores received in the applicability category. This was mainly because of difficulties in the areas of process turndown, decoupling, and retrofit due to the relative mechanical complexities of these processes. In general, dry processes received high scores in chemical process complexity and low scores in mechanical process complexity. The following processes were felt by the process evaluators to have potential for advances in FGD technology and were recommended for further evaluation.

Bergbau-Forschung - The B-F Process appears to have potential advantages over some FGD processes in the areas of dual SO_x/NO_x removal (up to 40% for NO_x), chemical simplicity, and reduced makeup water requirements. In addition, the process does not require reheat. No by-product sludge is produced, and the water requirements of the process are low.

Copper Oxide - The Copper Oxide Process has potential for solving some FGD problems in secondary pollutant environmental impact (no sludge is produced) and multipollutant removal (SO_x/NO_x).

Integrated Cat-Ox - The Integrated Cat-Ox Process was chosen for further evaluation because of its potential for reducing problems of cost, reliability, energy requirements, and secondary environmental impact. The process is simple both chemically and mechanically, and this could have significant cost and reliability advantages. Energy requirements are low since the liquor recirculation rate in the acid absorber is low and no stack gas reheat is required. The process produces acid as opposed to sludge and consequently has a minimal secondary environmental impact.

The Rohm & Haas Resin Adsorption Process was judged to have potential for enhancing or improving the concept of Sorption/Steam Stripping and is included as a process alternative in that Process/Subsystem Summary Paper. Another dry regenerable process receiving a high score, the Mitsubishi Manganese Oxide Process, was not recommended for further evaluation because of possibly severe environmental problems from manganese emissions.

Screening of FGD Subsystems

The FGD subsystems reviewed fell into the following process categories:

- Process/subsystems which regenerate calcium alkali solutions from $CaSO_4$,
- Processes/subsystems which regenerate sodium alkali solutions from Na_2SO_4,
- Processes/subsystems which are used to produce sulfur from SO_2, and
- Processes/subsystems which provide alternatives to commercial or developing technologies.

The initial screening evaluation criteria were not applied *per se* to these subsystems because many of the criteria were not applicable. Instead, the subsystems were examined in a rather qualitative manner to determine the extent of their applicability and if they offered potential economic or technological advantages when combined with existing FGD systems.

Lime and limestone regeneration processes regenerate calcium alkali solutions from sludge and can produce sulfuric acid or sulfur by-products. However, due to the chemical stability of the sludge, high fuel consumption and the use of a reducing gas are required. The high energy consumption and expensive construction materials make it unlikely that a regenerable lime or limestone process would be economically competitive with other regenerable processes. Thus, these systems were not recommended for further evaluation.

Sodium alkali regeneration subsystems convert by-product sodium sulfate to caustic soda or sodium carbonate solutions and produce either H_2SO_4 or sulfur. The Ionics electrolytic cell and the Rockwell International Reducing Section are subsystems that have been considered for this application. The evaluation indicated that the cost for regenerating the Na_2SO_4 by-product will more than likely be higher than the associated cost of disposal. Therefore it is unlikely that these subsystems will be applied to FGD systems except for specific installations where environmental regulations result in high costs for disposal of Na_2SO_4. The Rockwell International Reducing Section is discussed in the RI Process Summary Paper since the RI process was chosen for more detailed evaluation. The Ionics Subsystem was not recommended for further evaluation.

The following subsystems are used to convert SO_2 and/or H_2S to sulfur.

Claus	H_2S/SO_2 to sulfur
IFP	SO_2 to H_2S/SO_2 to sulfur
Allied	SO_2 to H_2S/SO_2 to sulfur
ASARCO	SO_2 to H_2S/SO_2 to sulfur
RESOX	SO_2 to sulfur

The Claus subsystem is in wide commercial use. This system, used to produce sulfur from a stream of H_2S, is not directly applicable to most FGD processes because the SO_2 removed from flue gases must first be reduced to H_2S before this technology can be applied. Therefore, the process has not been further evaluated.

The IFP and ASARCO Reduction Processes catalytically produce H_2S from SO_2 using H_2/CO reducing gas. Claus technology can then be used to produce sulfur from the resulting H_2S or in the IFP Process, a modified "liquid Claus." The major problem with applying the IFP and ASARCO technologies to FGD systems is producing the H_2/CO reducing gas. Currently, this gas is produced from natural gas. However, the decreasing availability and increasing cost of natural gas means that these technologies must be demonstrated using a coal-based reducing gas to remain viable subsystems in the future. Production of such a coal-based reducing gas will require the operation of a coal gasification system, which will increase both the chemical and mechanical complexity of these technologies. Consequently, further development of these processes has a secondary priority to the development of coal gasification.

A separate Process/Subsystem Summary Paper was not prepared for coal gasification. Coal gasification as a separate technology is being well supported by other government programs. However, none of these gasifiers has been integrated with an FGD unit. The extremely large number of gasification processes currently under development, many of which have vastly different operating conditions, combined with the differing requirements of FGD systems, make the selection of a gasification process separate from a specific FGD process or subsystem a meaningless exercise. Therefore, the potential of coal gasification for producing reducing gas for FGD systems was evaluated with regard to its applicability as a process alternative in the individual FGD Process/Subsystem Summary Papers.

The RESOX process reduces SO_2 with anthracite coal to produce sulfur. This process has been tested with a fully integrated FGD system. To lower cost, development work is underway to examine the use of bituminous coal as an SO_2 reductant. Since the RESOX process reduces SO_2 directly to sulfur, the need for a reducing gas and a Claus process are eliminated -- a distinct process advantage. RESOX units are applicable for retrofit installations and modularization, thereby making this process potentially very suitable for integration with FGD systems producing concentrated SO_2 as a by-product. This subsystem was recommended for further evaluation because of its wide applicability and its potential to produce sulfur without the need for reducing gas.

The following subsystems were considered as process alternatives which offer potential improvements to commercial or developing processes.

- Citrate Double Loop Regeneration (Citrate Buffered Absorption)
- Cocurrent Scrubbing (Lime/Limestone Wet Scrubbing)

- Dilute System Sulfate Removal (Sodium Based Double Alkali)

- Direct Production of Sulfur from $MgSO_3$ (Magnesia Slurry)

- Forced Oxidation (Lime/Limestone Wet Scrubbing or Sodium/Lime Double Alkali)

- Mass Transfer Additives (Lime/Limestone Wet Scrubbing)

- Sludge Stabilization (Lime/Limestone Wet Scrubbing)

5.4 Evaluation of Candidate Processes/Subsystems

The initial screening described above resulted in the selection of 19 candidate systems for further evaluation. Table 5-2 lists the processes recommended for further evaluation, along with a brief description of each process, its characteristics, and potential advantages. The objective of the detailed process evaluations was to identify specific RD&D opportunities for accelerating the commercialization of FGD technology and the specific benefits to be derived from these opportunities. The specific RD&D opportunities were then ranked and RD&D schedules and costs estimated.

To accomplish the objectives of this detailed candidate process/subsystem evaluation, the following tasks were performed:

- A set of detailed evaluation criteria was developed.

- Detailed technical and economic information on the 19 candidate processes was assembled in Process/Subsystem Summary Papers.

- The evaluation criteria were applied to the 19 candidate processes by each of the members of the technical Working Group and comparisons made with commercial and developing flue gas desulfurization technology.

- The Technical Working Group reached a consensus on a ranking of RD&D options including cost, schedules, and the benefits to be obtained in performing each option.

TABLE 5-2. PROCESSES SELECTED FOR FURTHER EVALUATION

Process	Description	Development status	By-Product or waste discharged	Potential advantages/benefits over commercial or developing processes
THROWAWAY				
Chiyoda Thoroughbred 121	SO_2 is absorbed into limestone slurry and $CaSO_3$ is oxidized to gypsum. Both of these operations are performed in the same vessel.	Pilot plant operation (750 acfm). Plans are under way to test the process at the 20 MW level at Scholtz.	Gypsum	1. Reduced costs compared to LS system because a single vessel is used for absorption, oxidation, precipitation. 2. Higher quality sludge compared to L/LS. 3. Sludge ponding may eliminate need for centrifuges.
Dowa Aluminum Sulfate	SO_2 is absorbed by solution of basic aluminum sulfate. The sulfite is then oxidized to sulfate. Limestone is used to precipitate gypsum.	Has been demonstrated abroad at up to 47 MW level, but not on coal-fired boilers. TVA-EPRI are considering a 10 MW demonstration at Shawnee.	Gypsum	1. Higher quality sludge compared to other double alkali systems. 2. Limestone is being used instead of lime as the regenerant.
Hölter	SO_2 is absorbed in a organic additive enhanced 0.5-10 wt. % solution of CaCl saturated with lime. Spent scrubber solution is oxidized to produce gypsum.	Hölter - 40 MW fully integrated on a coal-fired boiler	Gypsum	1. Lower reagent requirements compared to L/LS claimed. 2. Lower liquid circulation rates compared to L/LS. 3. Better quality sludge than L/LS. 4. Use of limestone instead of lime may offer additional cost advantages.
Kurabo	SO_2 is absorbed by an acidic solution of ammonium sulfate. Sulfite is oxidized to sulfate and gypsum is precipitated by adding lime.	Six units totaling about 200 MW have been put into operation in Japan.	Ammonium sulfate or gypsum-lime has been used to make up calcium	1. Can produce ammonium sulfate or gypsum. 2. Process operates in a dilute ammonia mode and is claimed to produce no ammonia sulfate fume. 3. Less susceptible to scaling and offers higher SO_2 removal than L/LS.
Lime/Limestone	SO_2 is absorbed by slurry of lime or limestone. Calcium sulfite and sulfate crystals precipitate in a reaction vessel. A 50% solids stream of sulfite and sulfate is disposed of by ponding.	Commercial	Calcium sulfite/ sulfate sludge	-
Sodium/Lime Double Alkali	SO_2 is absorbed by a soluble sodium-based alkali (NaOH or Na_2SO_3). The spent absorbent is reacted with lime to precipitate calcium sulfate, sulfate, and mixed crystals for disposal.	Commercial	Calcium sulfite/ sulfate sludge	-

(Continued)

TABLE 5-2. PROCESSES SELECTED FOR FURTHER READING (Continued)

Process	Description	Development status	By-Product or waste discharged	Potential advantages/benefits over commercial or developing processes
THROWAWAY (Cont'd)				
Sodium Based Throwaway Systems	SO_2 is removed by either a dry sodium alkali or a wet scrubbing solution. The wet process uses NaOH, Na_2CO_3, $NaHCO_3$, or some other alkali in a wet scrubber or spray dryer. The dry process uses nahcolite or trona to remove SO_2. The soluble sodium sulfite/sulfate compounds are then discharged.	Wet scrubbing - In the U.S. the 375 MW unit at Reid Gardner is in operation. In Japan there are some 800 plants with average capacity of about 7-20 MW. Dry Scrubbing - Most work has been pilot plant to date.	Soluble sodium sulfite/sulfate salts.	1. In areas where sodium is readily available, this process offers potential as a very low cost option. 2. The process is less complex than most processes and, therefore, may be more reliable.
WET REGENERABLE				
Ammonia/IFP	SO_2 is absorbed in a solution of aqueous ammonium sulfite and bisulfite. The spent sorbent is heated to 800°F to release SO_2 and NH_3. Part of the SO_2 is reacted with H_2/CO to produce H_2S. The total stream is passed through a liquid IFP reactor to produce molten sulfur.	The scrubbing operation has been tested at 2 MW at Calvert City, but did not clearly demonstrate fumeless operation. The brine recovery process has been demonstrated at 25 MW. Complete integration and demonstration on a coal-fired system has not been achieved.	Sulfur	1. High SO_2 removal efficiencies can be obtained. 2. Sulfur instead of sludge is the by-product.
Rockwell International Aqueous Carbonate Process (ACP)	The ACP uses an aqueous sodium carbonate solution to sorb SO_2 in a spray dryer. The dry sodium salts are collected and then reduced with coal or coke in a molten salt pool to form sodium sulfide. Sodium sulfide is dissolved and then carbonated to produce an H_2S gas for feed to a Claus unit.	Developing - A 100 MW demonstration plant is scheduled for start-up in 1978 as a retrofit to Niagara Mohawk Power Company's Huntley Station.	Sulfur	-
Citrate	The Citrate process is a buffered absorption process with citric acid as the buffer. The SO_2 laden liquor from the absorber is reacted with H_2S in regeneration reactors to form sulfur. H_2S is formed by reacting the product sulfur with a reductant such as CH_4, CO, or H_2.	Developing - A 60 MW demonstration plant at St. Joe Minerals Zinc Smelter in Pennsylvania is scheduled for start-up in 1978.	Sulfur	-

(Continued)

TABLE 5-2. PROCESSES SELECTED FOR FURTHER EVALUATION (Continued)

Process	Description	Development Status	By-Product or waste discharged	Potential advantages/benefits over commercial or developing processes
WET REGENERABLE (Cont'd)				
Magnesia Slurry	A circulating aqueous slurry of $Mg(OH)_2$ and $MgSO_3$ absorbs SO_2. Magnesium sulfite and sulfate crystals are precipitated and centrifuged. These solids are heated and decomposed to regenerate MgO and release SO_2. The SO_2 is best suited for sulfuric acid production.	Commercial	Sulfuric acid	-
Melamine	SO_2 is absorbed by a melamine slurry. The solids are filtered and fed to a fluid bed dryer. The solids are decomposed into SO_2, H_2O, and various melamine solids. SO_2 is sent to an acid plant. Since the SO_2-rich gas contains oxygen, sulfur production may be economically unattractive.	Bench Scale	Sulfuric Acid	1. Capable of high SO_2 removal efficiency (>99%). 2. No sludge disposal required. 3. Process energy consumption is potentially lower than the magnesia slurry process.
Sorption/Steam Stripping	SO_2 is absorbed in an aqueous solution of several potential sorbents (sodium citrate, ammonia, aluminum sulfate/aluminum chloride, ethylenediamine, glyoxylic acid, etc.). The SO_2-rich solution is then stripped with steam. Water is condensed and a gas containing ~95% SO_2 is produced. It can be converted to sulfuric acid or sulfur.	Though many of these processes have only been briefly tested, or are at the conceptual stage, their development to commercialization could be rapid. One facility could be built to test many sorbents.	Sulfur/sulfuric acid	1. Process simplicity. 2. Energy requirements are potentially very low.
Wellman-Lord	SO_2 is absorbed by an aqueous solution of Na_2SO_3 to form $NaHSO_3$. Regeneration involves heating the solution to reverse the absorption reaction. A concentrated SO_2 stream is produced which can be converted to sulfuric acid or sulfur.	Commercial	Sulfur/sulfuric acid	-

(Continued)

TABLE 5-2. PROCESSES SELECTED FOR FURTHER READING (Continued)

Process	Description	Development Status	By-Product or waste discharged	Potential advantages/benefits over commercial or developing processes
DRY REGENERABLE				
Bergbau-Forschung	SO_2 is adsorbed by a moving bed of char. The char is mixed with hot sand (1500°F) in a reducing atmosphere. Adsorbed SO_2 is released and can be converted to sulfuric acid or sulfur.	Has been successfully tested at the pilot plant and prototype level (45 MW) at Lunen in West Germany. The off-gas from the regenerator is sent to a modified Claus unit to produce elemental sulfur.	Sulfur/sulfuric acid	1. NO_x removal has been claimed. 2. No reheat required. 3. The process is simple chemically. 4. No sludge is produced. 5. Water requirements are low.
Copper oxide (Shell-UOP)	This process utilizes a solid copper oxide acceptor for SO_2 removal in fixed bed reactors. The copper oxide is converted to copper sulfate. The copper sulfate is reacted with a hydrogen reducing gas to produce copper, SO_2, and water. Copper is converted to its oxide state by reacting with oxygen in the flue gas.	Scale-up to 40 MW (in 1973) at the SYS refinery in Japan has been achieved. This was not a totally integrated unit and was placed on an oil-fired boiler. Additional tests are being carried out on an 0.6 MW unit at Tampa Electric.	Sulfur/sulfuric acid	1. NO_x removal is claimed. 2. No sludge is produced. 3. No reheat is required.
Integrated Cat-Ox	The Integrated Cat-Ox process uses catalytic oxidation of SO_2 to SO_3 and subsequent absorption of SO_3 in a sulfuric acid stream to produce a 75-80 percent acid product.	A 15 MW integrated system was successfully operated at Metropolitan Edison in 1967-1969. A 110 MW (utilizing the reheat method of retrofit) at Illinois Power's Wood River Plant operated only a limited time in 1973 and was unsuccessful. There are currently no plans for additional work.	Dilute sulfuric acid	1. Low cost process. 2. The process is simple mechanically and chemically. 3. Energy requirements are low since no reheat is required and L/G is low.
Sorption/Steam Stripping (Rohm & Haas Resin Adsorption Process)	SO_2 is adsorbed on a moving bed of ion exchange resin. SO_2 laden resin is transferred to a regeneration section where SO_2 is steam-stripped at about 260°F. The SO_2 is converted to sulfur or acid.	Bench scale to date.	Sulfur/sulfuric acid	1. Low energy requirements 2. Simple mechanically.
SUBSYSTEMS				
RESOX	RESOX is a process for the production of sulfur from an SO_2-rich gas. Crushed anthracite and SO_2 are mixed in a countercurrent reactor. The anthracite reduces the SO_2 to gaseous elemental sulfur.	Has been operated for a short time at the 20 MW level in an integrated Bergbau-Forschung/Foster Wheeler unit at Scholtz. A larger scale demonstration of the system is currently under way in Germany.	Sulfur	1. Eliminates need for reducing gas for sulfur production. This would reduce cost and complexity of many regenerable processes.

5.4.1 Development of the Evaluation Criteria

The following evaluation criteria were used by the Technical Working Group so that these process analyses would be conducted in a consistent and impartial manner. A sample evaluation form is presented in Appendix C.

Environmental and Energy Considerations

This category was designed to evaluate the potential of the process for reducing SO_2 emissions without resulting in major secondary pollution problems, and to evaluate process energy requirements. The considerations evaluated included:

1) Compliance with SO_2 Regulations - Does the process have the ability to meet future SO_2 emission standards with low, medium, and high sulfur coals?

2) Potential for Multipollutant Control - Can the process control one or more pollutants in addition to SO_2?

3) Secondary Pollution Problems - Are there potential or documented secondary air, water, or solid pollution problems associated with the processes?

4) Energy Intensiveness - How does the process compare with current commercial FGD processes in terms of chemical and electrical energy requirements?

Development Status

This category was designed to reflect ease of commercialization and potential for success. The inclusion of this category reflected the opinion that the more developed processes have less uncertainty in process configuration, problems, and economics. The following items were addressed:

1) Overall Development Status - How far has the process been developed and what sort of technical back-up data has been obtained? Has the process been integrated?

2) Use of Commercialized Technology - Does the process use technology that is proven?

3) Process Controllability - Is the process a complex one to control?

Economics and Technological Considerations

This category addressed what may be the most important parameter when making decisions among competing processes -- cost. The economic and technological consideration sections addressed the following points:

1) Capital Investment Costs - How did the process compare with the average capital cost for the processes considered?

2) Annualized Costs - How did the process compare with the average in terms of annualized (capital plus operating) costs?

3) Economic Sensitivity to Technological Factors - Is there potential for process costs to change substantially as the process is developed to commercialization?

Detailed economic estimates for all of the processes could not be obtained. When detailed estimates were unavailable, comparisons were made based upon similarity to other processes and the judgment of the evaluators.

Applicability

A final consideration in the evaluation was in the applicability of the process to utility and industrial situations, based upon the following factors:

1) Utility Applicability - Can the process be retrofitted and decoupled? Does it follow load well and produce an acceptable by-product? Are the processing steps generally acceptable to the utility industry?

2) Industrial Applicability - Can the process be retrofitted, decoupled, or modularized? Is the by-product readily marketable? Is the process applicable to small boiler operations?

3) Product Flexibility - What products can the process produce?

4) Regional/Site Considerations - Is the process applicable across a broad range of regions and sites?

5.4.2 Preparation of Process/Subsystems Summary Papers

Process/Subsystem Summary Papers were prepared for the Technical Working Group with accurate information on the processes selected for further study. Information was gathered from the published literature, from contacts with process vendors, and from other knowledgeable people in the field. This information was confirmed with independent engineering analysis. Economic estimates for both capital costs and annual operating costs were prepared by the Tennessee Valley Authority (TVA). In addition, comparative process costs were made available by EPRI. The basis for this economic analysis is presented in Table 5-3. As previously discussed, sufficient information was not available for TVA to prepare capital and operating cost tables for some of the processes. It was thus necessary to use engineering judgment in performing an economic analysis of the relative capital and annualized costs of these processes.

The Process/Subsystem Summary Papers were written in such a way that each point in the evaluation criteria was individually addressed. In addition, a section on process alternatives was provided to present these alternatives for research to the Technical Working Group. In those areas of the processes where the evaluation criteria could not be specifically addressed, attempts were made to provide sufficient information such that the Technical Working Group could apply engineering judgment in evaluating these processes. Process/Subsystem Summary Papers for each of the processes are presented in Appendix D.

5.4.3 Application of the Evaluation Criteria

Each member of the Technical Working Group independently evaluated the processes under consideration. Those evaluations were based upon data contained in the Process/Subsystem Summary Papers and on the evaluators' individual engineering judgment. After these independent judgments had been made, the group met and prepared consensus judgments of the processes under consideration.

It was apparent after some discussion that there was a strong correlation between the ranking of a process and its product: sludge, sulfuric acid, or sulfur. Thus, the group felt that it would be advantageous to rank the processes within these categories because the processes have regional and site-specific applicability. For example, the applicability of a sludge-producing process would be limited in a densely populated area with very costly land for disposal, the applicability of a sulfur-producing process would be greatly increased if a reductant such as hydrogen sulfide or hydrogen were readily available, and the applicability of a sulfuric acid-producing process would be increased in a fertilizer producing area.

TABLE 5-3. BASIS FOR PROCESS ECONOMIC ANALYSIS

500 MW New Utility Boiler

Midwest Location

Average Basis for Cost Scaling, Mid-1979

Power Unit Characteristics: 7000 hr/hr On-stream Time, 9000 Btu/kWh Heat Rate

Coal Burned: 1,500,100 tons/yr, 10,500 Btu/lb, 3.5% by wt. sulfur (dry), 16% ash.

Stack Gas Reheat to 175°F by Indirect Steam Reheat (if required)

Investment Requirements for Fly Ash Disposal Excluded

95% of Inlet Sulfur in Flue Gas

90% SO_2 Removal from Flue Gas

Additional Bases for the individual processes may be found in the Process/Subsystem Summary Papers in the Appendix.

Thus, each type of process has a significant area of unique applicability. In the absence of any constraints or special circumstances, the sludge-producing processes generally ranked the highest due to their simplicity. However, restricting further research to only sludge-producing processes would severely limit the overall applicability of FGD technology. Consequently, the Technical Working Group categorized the processes by their products, although it was understood that all three categories must be developed simultaneously in order not to limit the application of FGD technology. The categories decided upon for the candidate processes are presented alphabetically in Table 5-4.

The purpose of these evaluations was to eliminate processes which ranked low and showed no large potential for process improvement. The process evaluation provided a basis for agreement as to the advantages and disadvantages of each of the processes of additional development, it helped identify aspects of the processes which were in need of additional development, and it provided a means of comparing processes to identify the best opportunities for near-term RD&D.

TABLE 5-4. CATEGORIES OF CANDIDATE PROCESSES*

Throwaway Processes	Sulfuric Acid Processes	Sulfur Processes
Dowa	Integrated Cat-Ox	Ammonia/IFP AI/ACP
Hölter	Magnesia Slurry	Bergbau-Forschung
Kurabo	Melamine	Citrate
Lime/Limestone (including Chiyoda 121)	**Sorption/Steam Stripping	Shell/UOP
Sodium Carbonate Throwaway		Wellman-Lord
Sodium/Lime Double Alkali		Sulf-X

* RESOX subsystem was not categorized with the processes because it is an SO_2 processing unit and not a flue gas desulfurization process.

** Sorption/steam stripping is a generic category for several processes in wich SO_2 is sorbed in an aqueous or solid medium and stripped with steam at regeneration.

5.4.4 Priorities and Recommendations for RD&D Opportunities

After the Technical Working Group had reached concensus on the process evaluations, each member of the group submitted a list of the RD&D opportunities he felt were worthy of pursuit. These recommendations were consolidated and presented to the entire group. Each member of the Working Group ranked each option that had been presented as either an A (high priority), B (medium priority), or C (low priority) option. The list of priorities thus developed represented the Technical Working Group's RD&D recommendations. The Working Group felt that future RD&D should be focused on improving the economics and applicability of systems that have been or are being demonstrated on large-scale equipment. Because of the emphasis on finding near-term solutions to existing problems, many of the RD&D recommendations were to further investigate process subsystems or process alternatives. These recommendations, in general, concerned RD&D categories that have potentially widespread application, especially in wet throwaway FGD processes.

The Technical Working Group next set about the task of estimating RD&D schedules and costs for the RD&D options. After consideration of ongoing RD&D efforts by other organizations, the group concurred on a set of RD&D recommendations, complete with estimated costs and scheduling. The projected RD&D costs were estimated to represent total costs for the completion of a project and include all costs for capital expenditures along with support items such as testing and instrumentation. This final list of RD&D options is presented graphically in Figure 5-2. This figure also indicates coordination with other ongoing programs.

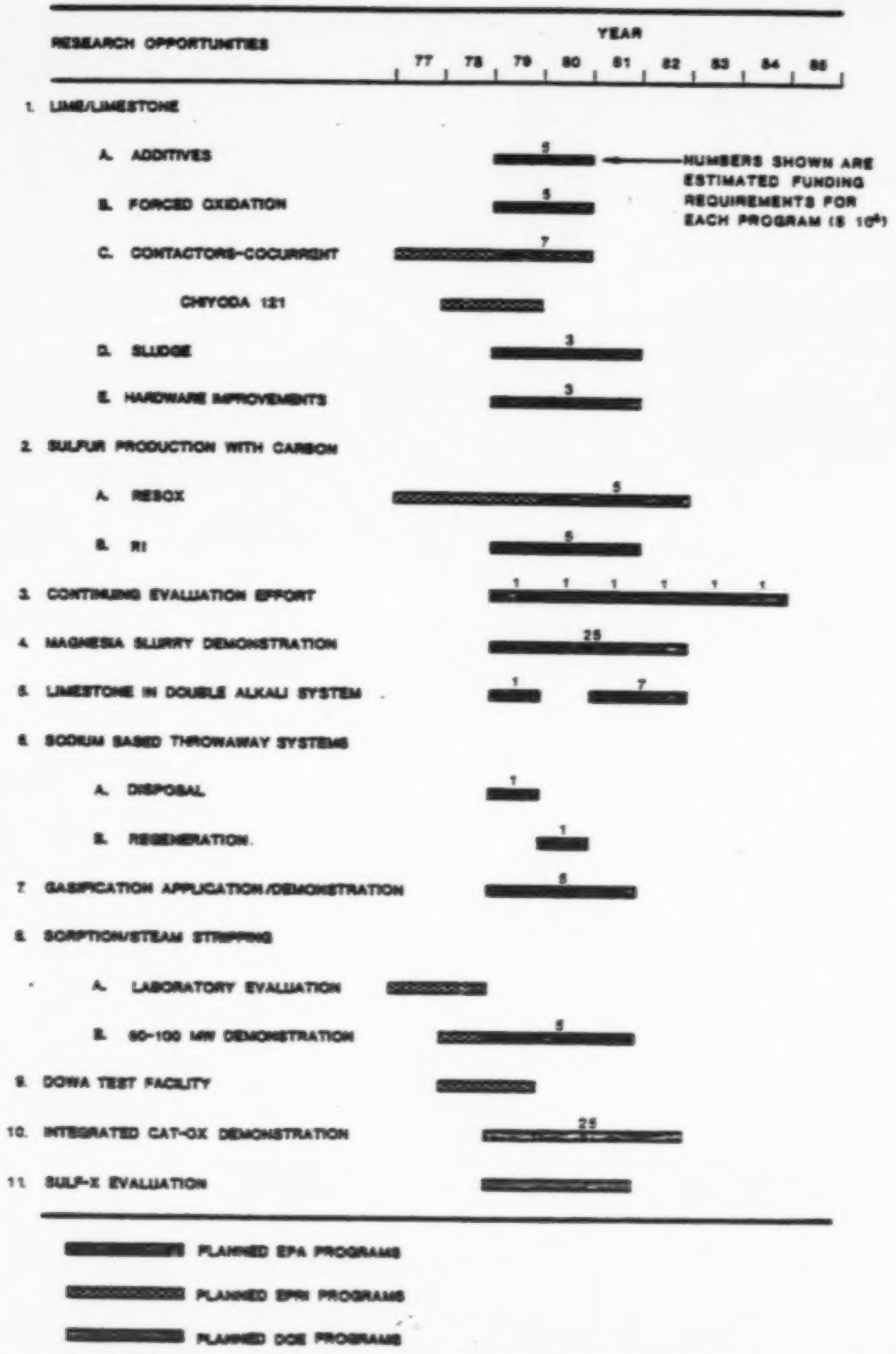

FIGURE 5-2. RD&D Priority List - Schedule and Costs (millions of dollars)

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APPENDIX A

EVALUATION FORMS AND CRITERIA FOR CANDIDATE PROCESS/SUBSYSTEM SELECTION

This appendix contains the detailed evaluation forms used in screening the comprehensive process list to arrive at a set of candidates for further RD&D funding. This evaluation was performed in order to select those processes which appeared to offer the most potential for improvements over currently commercial and developing FGD processes for further, more detailed evaluation.

INITIAL SCREENING EVALUATION CRITERIA FOR CANDIDATE PROCESSES/SUBSYSTEMS

I. Minimum Requirements — Go/No Go

Processes/subsystems which fail to meet any of these requirements will not be considered further

A. A process/subsystem must be able to achieve compliance with the minimum assumed future NSPS for SO_2

B. A process/subsystem must be capable of being demonstrated by 1985

C. A process/subsystem must be applicable to treating flue gases from combustion of coal

D. Adequate information must be available to enable process/subsystem evaluation

II. Environmental and Energy Considerations — 30 points

A. Compliance with SO_2 Regulations (Assumes 0.4 lb $SO_2/10^6$ Btu) — (6 points)
   - 6 - potential to comply with future regulations with high sulfur coals (96%)
   - 4 - potential to comply with future regulations with medium sulfur coals (94%)
   - 2 - potential to comply with future regulations with low sulfur coals (80%)

B. Potential for multipollutant removal — (3 points)
   - 3 - more than one
   - 1 - one
   - 0 - none

C. Performance growth potential — (3 points)

D. Secondary pollutant problems — (3 points)
   - 3 - none
   - 2 - minor
   - 0 - major

INITIAL SCREENING EVALUATION CRITERIA FOR CANDIDATE PROCESSES/SUBSYSTEMS (Continued)

E. Relative Energy Requirements
Since material and energy balances will not be available for many of these processes, the following qualitative rating factors will be used:

1) Reheat (3 points)
   - 3 - none
   - 2 - possibly
   - 1 - from saturation (125°F) to 175°F

2) Reducing Gas (3 points)
   - 3 - none
   - 1 - CO and H_2
   - 0 - H_2 only

3) L/G Ratio, Pressure Drop (3 points)
   - 3 - low
   - 1 - medium
   - 0 - high

4) Other Energy (3 Points)
   - 3 - low
   - 1 - medium
   - 0 - high

F. Raw Material Requirements (3 points)
- 3 - uses less than 2 that are readily available
- 2 - uses less than 2 that are readily available
- 0 - uses more than 2 that may not be readily available

III. Development Status 25 points

A. State of development (10 points)
- 10 - demonstration (30 MW) coal-fired
- 8 - demonstration (30 MW) oil-fired
- 7 - prototype (10-30 MW) coal-fired
- 5 - prototype (10-30 MW) oil-fired
- 4 - pilot (1-10 MW) coal-fired
- 3 - pilot (1-10 MW) oil-fired
- 2 - bench scale
- 1 - conceptual

INITIAL SCREENING EVALUATION CRITERIA FOR CANDIDATE PROCESSES/SUBSYSTEMS (Continued)

B. Degree of Integration (5 points)
- 5 - totally integrated
- 3 - sorption and regeneration integrated
- 0 - nothing integrated

C. Use of currently commercialized technology (5 points)
- 5 - in all process sections
- 3 - in at least two process sections
- 2 - in one process section
- 0 - not at all

D. Scale-up problems (5 points)
- 5 - no apparent problems
- 2 - potential problems with complexity or scale-up of a new or unique processing step
- 0 - potential scale-up problems in several areas

IV. Economic and Technological Considerations 25 points
(applied to major sections and subsystems)
Capital requirements may be estimated by considering:

A. Relative Chemical Complexity (15 points)
- 15 - simple, workable
- 10 - complex, workable
- 5 - simple, questionable
- 0 - complex, questionable

B. Relative Mechanical Complexity (10 points)
- 10 - simple
- 5 - moderately complex
- 0 - very complex

V. Applicability 20 points

A. Suitability for Utility Applications (10 points)

1) Separability of Process Steps (3 points)
- 3 - can be easily decoupled
- 1 - difficult decoupling
- 0 - decoupling not practical

INITIAL SCREENING EVALUATION CRITERIA FOR CANDIDATE PROCESSES/SUBSYSTEMS (Continued)

2) Load Following Capability (3 points)
   - 3 - follows load changes rapidly
   - 1 - follows load changes slowly
   - 0 - process sections do not readily follow load changes

3) Retrofitability (2 points)
   - 2 - easy to retrofit
   - 1 - will require minor modifications
   - 0 - significant problems

4) By-product utilization/marketability (2 points)
   - 2 - readily marketable
   - 1 - marginally marketable
   - 0 - unmarketable

B. Suitability for Industrial Application 10 points

1) By-product utilization/marketability (3 points)
   - 3 - readily marketable
   - 1 - marginally marketable
   - 0 - unmarketable

2) Ability to modularize the process (3 points)
   - 3 - suitable for small (<10 MW) modules
   - 1 - suitable for medium (10-40 MW) modules
   - 0 - suitable for (>40 MW) modules

3) Separability of Process Steps (2 points)
   - 2 - can be easily decoupled
   - 1 - difficult decoupling
   - 0 - decoupling not practical

4) Retrofitability (2 points)
   - 2 - easy to retrofit
   - 1 - will require minor modifications
   - 0 - significant problems

APPENDIX B

INFORMATION SURVEY PAPERS

This appendix contains the information that was used in the initial screening of processes. This screening was done to arrive at those processes felt to have significant potential for improvements over currently commercial and developing processes. The evaluation criteria presented in Appendix A were applied based upon the information provided in the Information Survey Papers in this appendix.

AGGLOMERATING CONE PROCESS

Process/Subsystem Description - Potassium carbonate, anhydrous ammonia or phosphate rock are added to flue gas before entering the scrubber. As flue gas enters the scrubber (agglomerating cone) the compressible fluid accelerates. The acceleration of the particles in the gas is a function of their sizes. The particles, accelerating at different rates, collide and bind together with SO_2 absorption onto the agglomerate. A fine mist injected at the top of the cone provides additional binding targets. Agglomerated substances are washed out the bottom. Clean flue gas is passed through a mist eliminator before it is exhausted out the stack.

Environmental and Energy Considerations - A demonstration unit has shown 90% removal of SO_2. Data on removal of other pollutants were not available. Sludge disposal may pose an environmental problem, although some thought is being given to using phosphate rock solution in the liquid injection and recovering the effluent in the form of a fertilizer. Little is known about the energy requirements for the process, but the pressure drop across the system is reported to be low.

Development Status - A pilot plant (about 1 Mw) unit has been tested using coal-fired flue gas. The technology in use is somewhat novel, and scale-up problems can be expected.

Economic and Technological Considerations - The system appears fairly simple. There are no moving parts in the system, and there is no regeneration equipment. The absence of regeneration reduces overall complexity.

Applicability - This system appears suitable for use in utility and industrial applications. Load following capabilities should be reasonable, and retrofit should be easy. The sludge will have to be treated before it can be marketed as a by-product, however.

Summary and Conclusions - Consideration of this process is hindered by lack of information. Energy requirements are minimized; the system is fairly simple; and a potentially marketable by-product results. This process is not recommended for further consideration at this time.

References - FE-218.

ALKALINE ASH SCRUBBING PROCESS

Process/Subsystem Description - In the alkaline ash scrubbing process, the natural alkalinity of ash is used to sorb SO_2 in a wet throwaway system. The ash may be collected in the scrubber or collected in a precipitator, slurried and transferred to the absorber. The scrubbing technology is similar to that used to control particulate emissions, except for the sorbent addition and sludge handling operations. Supplementary lime or limestone may be added to improve SO_2 removal.

Environmental and Energy Considerations - Because of the limited alkalinity in the fly ash, SO_2 removal is generally low (less than 50%) but removal efficiencies as high as 80 to 85% have been reported in small scale units. Higher removal efficiencies may be possible. Particulates are also removed. Disposal of the sludge produced poses secondary pollution problems more severe than those resulting from the disposal of sludge from conventional lime/limestone systems because of the presence of heavy metals and organics in the fly ash. Energy requirements are similar to those for particulate scrubbing. Values of L/G from around 13 to 80 and of pressure drop from 4 to 30 inches of water have been reported. A relatively high L/G would probably be required for good SO_2 removal. The stack gas must also be reheated from saturation. The principal raw material used is the fly ash produced from combustion of the coal. Small amounts of lime or limestone may also be added for pH control or to improve SO_2 removal.

Development Status - Particulate/SO_2 scrubbers using alkaline ash as sorbent are installed on approximately 2500 MW of utility capacity in the western U.S. Most of these scrubbers were originally designed for particulate control only. Two scrubbers on two 362 MW units are currently in operation at the Colstrip Station of Montana Power Company, achieving New Source Performance Standards (1.2 lb $SO_2/10^6$ Btu) by feeding flue gas containing both fly ash and SO_2 directly to the scrubber. A full scale 450 MW unit is planned at the Milton R. Young Station of Square Butte Electric Cooperative. Data for design of this unit were obtained from operation of a 5000 acfm pilot plant. The process uses commercial technology and has been integrated. Scale-up problems could be severe because of the variability of the fly ash composition due to potential problems with applicability of data from one system to another.

Economic and Technological Considerations - The ash scrubbing process is quite complex. Because the composition of fly ash varies considerably and the amount of ash produced depends on boiler type, SO_2 removal efficiencies could fluctuate. The characteristics of sludge also vary as the fly ash varies. Scaling and corrosion problems could be severe.

Applicability - The process is applicable only to units burning coal with a low sulfur content, high ash content and high degree of alkalinity in the ash. Sludge that will be difficult to dispose of in an environmentally acceptable manner will be produced as a by-product. Retrofits and industrial modularization may also be difficult.

Summary and Conclusions - This process scored slightly below average compared to other throwaway processes. It is fairly well developed, but scored about average in Environmental and Energy Considerations, a little below average in Chemical and Mechanical Complexity, and quite low in Applicability. This process has an advantage in using a waste product as a raw material, but is limited to use with coals having a high alkaline ash content and low sulfur content. SO_2 removal is more difficult than in lime/limestone scrubbing. Because of low pH, leaching of heavy metals from the fly ash can occur. This process is not recommended for further evaluation.

References - HA-650, NE-206

ALKALIZED ALUMINA PROCESS

Process/Subsystem Description - In the Alkalized Alumina Process SO_2 is absorbed on sodium aluminate pellets ($NaAlO_2$) in a fluidized bed at 570-660°F. The absorbent is constantly withdrawn and regenerated with hydrogen reducing gas produced by steam reforming of natural gas, LPG, or fuel oil; or potentially by coal gasification. H_2S is evolved in the regeneration step. Part of the H_2S is burned to SO_2; the remaining H_2S and the SO_2 are sent to a Claus plant for production of elemental sulfur.

Environmental and Energy Considerations - Small-scale tests have indicated that 90% removal of SO_2 can be achieved with a reasonable amount of absorbent. The process has been found to be less energy-consuming than some comparable methods, but the regeneration step requires a hydrogen reducing gas and occurs at a high temperature. Stack gas reheat is not required although the flue gas may have to be heated to absorption temperature in retrofit applications. Investigations to date have utilized natural gas, LPG or fuel oil for hydrogen production. It is unlikely that this will prove to be viable long term and coal gasification would probably become the method of choice for supplying reducing gas. The absorbent is fabricated by reacting solutions of Na_2CO_3 and $Al_2(SO_4)_3$ and then heating to form $NaAlO_2$.

Development Status - The process was developed at the bench scale by the U.S. Bureau of Mines. Some work was also done at power plants in England. Development of the process has now ceased because of severe problems with attrition of the alkalized alumina pellets.

Economic and Technological Considerations - The process is complex both chemically and mechanically. Deterioriation of the alkalized alumina pellets over an extended period of cycling is a major problem in this process. The main cause of this disintegration of the pellets is apparently the change in crystal structure that occurs in the cycle of absorption to regeneration and back again. Mechanical attrition probably also contributes to the disintegration.

Applicability - Process applicability suffers from lack of turndown, retrofitability, and ability to modularize. Retrofit applications may require some modification; for example, the fluidized reactor may have to be operated at a lower temperature. The process produces sulfur as a by-product.

Summary and Conclusions - The Alkalized Alumina process scored low compared to other dry processes and seems to have little chance of further development. Technical problems associated with attrition of the alumina pellets proved insurmountable in previous development work and caused the developers to reject the process as technically unfeasible. This process is not recommended for further consideration.

References - SL-070, TO-058, CA-327

ALLIED CHEMICAL ELECTRODIALYSIS PROCESS

This process is based on the scrubbing of flue gas with a sodium sulfite and sodium hydroxide absorbent solution similar to that of the Wellman-Lord process. Regeneration is accomplished in an electrolytic cell employing cation-permeable and bipolar membranes which split the bisulfite solution from the scrubber into a basic stream suitable for return to the scrubber and an acid stream which is stripped for SO_2 recovery. Allied reports that preliminary studies have predicted lower operating and capital costs for the system than the lime/limestone scrubbing or the Wellman-Lord process. Due to the early stage of development of the process, Allied was reluctant to release more information concerning details of the process in a telephone conversation. Therefore, the process was not recommended for further evaluation.

References - CH-424, FL-086

ALLIED REDUCTION PROCESS

Process/Subsystem Description - In this process a concentrated SO_2 stream, such as produced by the Wellman-Lord process, is heated, mixed with a correct amount of methane and passed over a catalyst. Part of the SO_2 is reduced to sulfur and part to H_2S. The sulfur is condensed and the remaining H_2S-SO_2 mixture is fed to a modified Claus unit. Efforts are underway to evaluate applicability of the process with an H_2/CO reducing gas instead of methane.

Environmental and Energy Considerations - The Allied Process has only been demonstrated using methane as a reductant. In view of decreasing methane availability, the process must be demonstrated using coke or coal as a reductant in order to remain a viable process in the future. Early reports indicate that the reactor may be adaptable to a H_2/CO mix which could be supplied by coal gasification.

Development Status - The process is being installed on a 115 MW plant in a system integrated with the Wellman-Lord Process based upon methane as a reducing agent.

Economic and Technological Considerations - The use of methane for reducing gas makes this process a major contributor to the operating expense of an integrated system. The use of an H_2/CO mix from coal gasification should be demonstrated.

Applicability - No limitations have been discussed for application of this system to new or retrofit installations. However, if the process cannot be successfully operated with an H_2/CO reducing gas, methane availability may limit applicability.

Summary and Conclusions - This subsystem was developed to reduce SO_2 to H_2S and sulfur by using a methane based reducing gas. The remaining H_2S would also be converted to sulfur by a Claus unit. In view of the decreasing methane availability this process must be demonstrated using a coal based reducing gas. This process is not recommended for further evaluation in lieu of a more direct subsystem for converting SO_2 to sulfur.

References - OT-R-051

AMMONIA BISULFATE (ABS)

Process/Subsystem Description - SO_2 is absorbed in a concentrated solution of ammonium sulfite. The solution is reacted with NH_4HSO_4 in combination with evaporation to produce concentrated SO_2 gas and ammonium sulfate solids. Ammonium sulfate is thermally decomposed as a melt at 700°F to NH_3 gas and NH_4HSO_4 melt. Net sulfate produced in the scrubber can be reduced to NH_3 and SO_2 by adding sulfur to the decomposer. Heat for thermal decomposition can be provided by electric power or clean fuels. Potential for the formation of an ammonium salt fume requires that the scrubber be designed with careful control of pH and/or a wet electrostatic precipitator.

Environmental and Energy Considerations - The process should be capable of SO_2 removal efficiencies of 90% or greater, but does not appear to have potential for multipollutant removal. NH_3 fume formation may be a problem even with complex scrubber design. Energy requirements are comparable to those for Wellman-Lord and MgO scrubbing. They include steam for evaporative crystallization as well as electric power or fuel for sulfate decomposition. Gas reheat is also required. Makeup ammonia or NH_4HSO_4 will be required as a raw material.

Development Status - This process has been tested at a semi-integrated 1000 cfm pilot plant by TVA, but development efforts were discontinued in 1976. Some use of novel process technology would be required, and scale-up problems may be encountered.

Economic and Technological Considerations - This process is relatively complex, chemically and mechanically. Complexity of regeneration will add to cost. Scrubber design is complicated by NH_3 volatility and possibility of fume formation. Prescrubbing is necessary to exclude chlorides from the regeneration system and to permit adequate fume control. Alternative methods of sulfate removal include purge as marketable ammonium sulfate and neutralization with lime to give gypsum waste. The high temperature decomposition step will cause problems with materials of construction.

Applicability - This process appears to be generally applicable for utility or industrial use. It can be turned down, retrofitted, and modularized. Process sections can be decoupled by provision of intermediate storage between scrubbing and regeneration. Since concentrated SO_2 is produced as a by-product, (which may be used to produce H_2SO_4 or sulfur) applicability is not limited by by-product marketability.

Summary and Conclusions - This process scored low compared to other wet regenerable processes. It scored high in applicability, but low in the other categories. Energy requirements for the process are comparable to those for Wellman-Lord and MgO scrubbing. This process has an advantage over the Wellman-Lord process in sulfate handling, but the required scrubber complexity and the possibility of ammonia fume formation are serious disadvantages. This process is not recommended for further consideration.

References - RO-333

AMMONIA EVAPORATIVE CRYSTALLIZATION

Process/Subsystem Description - SO_2 is absorbed in a concentrated solution of ammonium sulfate. The solution is evaporated under vacuum to produce ammonium sulfate solids and concentrated SO_2. Sulfate is removed by purging ammonium salts or by neutralizing with lime to produce gypsum.

Environmental and Energy Considerations - Ammonia fume formation may be a problem, even with complex scrubber design. Steam requirements could be as much as a factor of two less than Wellman-Lord. Some ammonium sulfate or gypsum would be produced.

Development Status - This process is still at the conceptual stage.

Economic and Technological Considerations - Scrubber design and operation is complicated by NH_3 volatility and the possibility of fume formation. NH_3 volatility may also complicate evaporator design, requiring lower temperatures and pressures.

Applicability - There appears to be no technical factors that would seriously limit applicability of this process for utility or industrial use.

Summary and Conclusions - This process appears to have lower energy requirements than the NH_3 bisulfate, NH_3/IFP, and Wellman-Lord processes. It also may be superior to Wellman-Lord in sulfate handling. However, the problem of fume formation is serious. This process was not evaluated because of its conceptual state of development.

References - RO-333

AMMONIA/IFP (Catalytic, Research Cottrell)

Process/Subsystem Description - SO_2 is absorbed in ammonium sulfite solution at carefully controlled pH. The rich solution is evaporated to give a gas containing H_2O, SO_2, and NH_3. Residual solution containing ammonium sulfate is heated to 700°F and decomposed to NH_3 and SO_2 in a melt of ammonium bisulfate with added sulfur. Gas from the decomposer is reacted with H_2/CO to eliminate SO_3, then mixed with gas from the evaporation and reacted with H_2/CO to give two moles H_2S per mole SO_2. The total gas stream is passed through a liquid IFP reactor at about 300°F to produce molten sulfur and gaseous NH_3. The ammonia is recovered by absorption, then returned to the scrubber.

Environmental and Energy Considerations - Ammonia fume formation may be a problem even with complex scrubber design. Concentrated solution aggravates the problem of fume formation, but is required to minimize the steam requirements for evaporation. H_2/CO is required for reducing SO_2 to sulfur and is also used to provide heat for sulfate decomposition. Energy requirements are larger than those for the Citrate process. The flue gas must be reheated. The L/G and pressure drop of the scrubber are relatively low. Raw material required is ammonia.

Development Status - The process has been tested at the prototype scale (20 to 30 Mw) in France and Japan. Integration of the process has been very limited. Except for the scrubber, the process uses current technology. Scale-up problems may be difficult to solve, especially for the scrubber.

Economic and Technological Considerations - The process incorporates a large number of operations that will make it complex both chemically and mechanically. Scrubber design is complicated by ammonia volatility and the possibility of fume formation. Prescrubbing is necessary to exclude chlorides from regeneration. Alternative methods of sulfate removal such as ammonium sulfate purge and marketing or lime regeneration to produce gypsum would simplify the process at the expense of adding a by-product. Materials of construction have been a problem.

Applicability - The process is suited quite well for utility and industrial application. It can be turned down, retrofitted, and decoupled. Industrial modularization is also feasible. The by-product sulfur is marketable.

Summary and Conclusions - The Ammonia/IFP process rated as above average among the wet regenerable processes. Ammonia plume formation is a serious problem with most ammonia scrubbing processes. This process, however, may have potential for controlling plume formation by careful process control (Catalytic) or by the use of a wet electrostatic precipitator (Research Cottrell). This process is recommended for further evaluation.

References - RO-333

AMMONIA SCRUBBING/H_2SO_4 ACIDULATION

(COMINCO, AMMSOX)

Process/Subsystem Description - Flue gas is scrubbed with ammonia, producing ammonium sulfite and bisulfite. Strong H_2SO_4 is added to the scrubber effluent solution in the acidifier where the H_2SO_4 reacts with the ammonium sulfite and bisulfite to produce ammonium sulfate and evolve SO_2. The acidified solution is stripped with air to remove most of the residual SO_2. Ammonia is then added to neutralize any residual acidity, and the ammonium sulfate is removed in a crystallizer. The SO_2 evolved is converted to H_2SO_4 in a contact-type sulfuric acid plant. Some of the H_2SO_4 produced is used for acidulation; any excess is sold.

Environmental and Energy Considerations - An SO_2 removal efficiency of 96% has been claimed for the process in treating waste gases from sulfide ore smelting operations. No other pollutants are removed. As with other ammonia scrubbing processes, plume formation is a serious problem. Disposal of the ammonium sulfate if it cannot be sold could also be a problem. Energy requirements should be relatively low. Gas reheat will be required, but no reducing gas is used and L/G and pressure drop should be relatively low. An air stripping column is required in addition to the ammonia scrubber, however. Ammonia is required as a raw material, along with H_2SO_4 or the raw materials required to produce H_2SO_4 from SO_2 in an acid plant.

Development Status - The process was developed by Cominco in the 1930's to treat waste gases from sulfide ore smelting operations. It is being used commercially in smelter and sulfuric acid plants, but has not been tested on a large scale on a power plant in North America. TVA has made tests in a 4000 scfm, coal-fired plant. The process uses current technology and has been integrated. Some scale-up problems may be experienced.

Economic and Technological Considerations - This process is more complex, both chemically and mechanically, than the sodium double alkali process. Scrubber design is complicated by the volatility of the ammonia and the possibility of plume formation. Corrosion could be a problem in all process sections. In order to maximize sulfuric acid production the scrubber should be designed and operated to produce more bisulfite than sulfate.

Applicability - Operating characteristics of this process should not seriously limit its applicability for utility or industrial applications. The process can be turned down, retrofitted, and modularized. Process sections can be decoupled. Applicability is limited to areas where a market for ammonium sulfate exists. The SO_2 may be converted to H_2SO_4 on site so that it can be used in the acidulation stage.

Summary and Conclusions - This process did not score well compared to other throwaway processes due to its overall complexity. In addition, secondary pollution from ammonia plume formation is a serious problem. Applicability of the process is limited to areas where a market for ammonium sulfate exists. This process is not recommended for further consideration.

References - CA-327, MC-296, SL-070

AMMONIA SOLUTION DOUBLE ALKALI PROCESS

Process/Subsystem Description - This process is analagous to the Calsox process. SO_2 is absorbed in $(NH_4)_2SO_3$ solution. Spent scrubber solution is regenerated at pH 10 with lime to produce $CaSO_3/CaSO_4$ solids and aqueous ammonia. The scrubber feed solution is softened by reaction with the scrubber product to precipitate $CaSO_3$ solids which are separated before scrubbing.

Environmental and Energy Considerations - Good SO_2 removal should be possible. Secondary pollution problems could result from disposal of the waste products. The use of relatively dilute ammonium sulfite solution (0.2-0.5 molar) should minimize, but not eliminate, ammonium salt fume formation. Energy requirements would be comparable to those for other scrubbing systems. Lime and ammonia are required as raw materials.

Development Status - This process is essentially at the conceptual stage.

Economic and Technological Considerations - This process is suitable for almost any level of oxidation. Minimal NH_3 makeup is required. Chlorides may require a solution purge. Volatility of ammonia may present on-site problems during the regeneration step. Adequate containment or venting is required.

Applicability - No limiting factors are apparent.

Summary and Conclusions - Kurabo offers a more attractive alternative than this process for fume-free operation using NH_3 scrubbing with gypsum production. This process has the flexibility of operation at high levels of oxidation not offered by sodium/lime double alkali, but it may also have a significant problem with fume formation. Lime must be used for regeneration. Since the process is conceptual, it is not recommended for further evaluation.

References - RO-333

AMMONIA VAPOR DOUBLE ALKALI
(UGINE KUHLMAN, NIPPON KOKAN)

Process/Subsystem Description - SO_2 is absorbed in ammonium sulfite solution. The absorption step is followed by forced oxidation. Spent scrubbing solution is then regenerated with lime at 175-190°F and the NH_3 is volatilized. Moderate ammonium salt concentration (1-2 molar) is required to minimize steam requirements for ammonia stripping. Ammonia vapor is recovered and returned to the scrubber.

Environmental and Energy Considerations - Adequate SO_2 removal should be possible. The process does not appear to have potential for multipollutant removal. At moderate salt concentrations ammonia fume formation could be a significant problem. Other secondary pollution problems could result from disposal of the waste solids. Energy requirements may be slightly higher than those for the sodium double alkali process. Reheat is required but L/G and pressure drop should be relatively low. In addition, steam is required to heat the solution and strip out ammonia. Ammonia and lime are required as raw materials.

Development Status - The process was tested at 25 MW coal-fired prototype by Ugine Kuhlman/Weirstam in France in 1974. Nippon Kokan has tested a 75,000 cfm system on a sintering plant (1973-76). However, the process has not been fully integrated. New technology is required in the scrubber in the forced oxidation step. Some scale-up problems are anticipated.

Economic and Technological Considerations - The process appears to be more complex chemically and slightly more complex mechanically than the sodium/lime double alkali process. Scrubber design is complicated by ammonia volatility and the possibility of fume formation. The process is effective at any level of scrubber oxidation but requires lime for regeneration. Ugine Kuhlman used NO_2 as a gaseous catalyst for oxidation. Chlorides can be purged as a $CaCl_2$ solution.

Applicability - This process appears to be generally applicable for utility or industrial use. It can be turned down, retrofitted, and modularized. Process sections can be decoupled. Applicability may be limited by the need to dispose of large quantities of solid waste.

Summary and Conclusions - This process scored about average compared to other throwaway processes. It has good applicability but is more complex than some of the other throwaway processes and scored lower in Environmental and Energy Considerations. Fume formation is a significant problem; the Kurabo ammonium sulfate process is superior in avoiding fume formation. This process is suitable for operation at any level of oxidation, unlike the sodium/lime double alkali process. This process is not recommended for further evaluation.

References - BE-466, AN-147.

AQUACLAUS PROCESS

Process/Subsystem Description - In this process, SO_2 is absorbed in a solution of sodium phosphate at pH 3.5-4.5. Elemental sulfur is produced by reaction of the solution with H_2S. The sulfur is separated from the solution by air flotation, melting, and decanting. H_2S is produced by reaction of sulfur with H_2/CO or methane. Sulfate is removed by refrigerated crystallization of Glauber's salt.

Environmental and Energy Considerations - The AQUACLAUS Process is capable of excellent SO_2 removal (99%). No potential for multipollutant removal exists, though. Secondary pollutant problems consist only of a sodium sulfate solid waste which may possibly be marketed. Some reheat of the flue gas is required and a reducing gas is needed. Other energy requirements are low. The L/G and therefore the pressure drop for the scrubber is high. The raw material required is sodium phosphate.

Development Status - The process has been tested in a 100 cfm scrubber followed by a sulfur generator. The process has not been integrated. There is some use of noncurrent technology in the solution regeneration process section. A few scale-up problems are expected because of the relatively undeveloped status of the process.

Economic and Technological Considerations - The chemistry involved in the scrubbing step of the process is simple and well understood. However, the chemistry of the regeneration/SO_2 conversion step is somewhat complex. Mechanically,the scrubber is simple in design. The regeneration/SO_2 conversion equipment is very complex.

Applicability - The process does not appear to have problems that would limit its applicability to utility and industrial application. Turndown and retrofit should be possible, as well as industrial modularization of the equipment. However, decoupling of the absorption and regeneration is not economically feasible because of the high L/G and low buffer capacity of the solution.

Summary and Conclusions - The AQUACLAUS process rated average among the wet regenerable processes. The rating was due primarily to the process' need for a reducing gas and the process' relatively undeveloped state. Advantages of the process include reduced buffer losses relative to the Citrate process and excellent SO_2 removal ability. Disadvantages include possible scale-up problems, the need for a reducing gas, and large liquid-to-gas ratios in the absorber. This process is recommended for further consideration in conjunction with the citrate process.

References - FE-218

ASAHI CHEMICAL PROCESS

Process/Subsystem Description - An Na_2SO_3 solution containing Fe^{+2}·EDTA is used to absorb SO_2 and NO_x in this process. After prescrubbing for hydrogen chloride and particulate removal, the flue gas is contacted with the scrubbing solution in an absorber. It is then passed through a mist eliminator and a reheater before being exhausted from the stack. A portion of the absorber effluent is treated in a complex series of chemical processing and separations steps to produce gypsum and sodium sulfate by-products and to regenerate the sorbent.

Environmental and Energy Considerations - Bench-scale testing on flue gas from oil-fired boilers (150-250 ppm NO_x, 1250-1550 ppm SO_2) resulted in more than 99% removal of SO_2 and 80-85% removal of NO_x. Particulates and hydrogen chlorides are also removed. Disposal of by-products may prove to be an environmental problem. The L/G ratios in the absorber are 65-100 gal/Mcf. High L/G ratios indicate the potential for high energy requirements associated with pumping and high pressure drop. Relatively large amounts of energy are also required in the thermal crackers operating at 930°F for sorbent regeneration. Some of the heat generated in the crackers is used for reheating the clean flue gas and in drying solids, but the remainder is lost. Raw material requirements include limestone, $FeSO_4 \cdot 7H_2O$, EDTA, and Na_2CO_3.

Development Status - This process has not been tested on flue gas from a coal-fired boiler. It has been tested as an integrated unit in a bench-scale unit treating 24-35 scfm of flue gas from a residual oil-fired boiler. The absorption, crystallization, and decomposition sections have been tested in a bench-scale unit treating 300-350 scfm. Currently, commercialized technology is used throughout the process. A potential for scale-up problems exists because of the fact that the process has not been tested on coal at the bench-scale level and because of overall process complexity.

Economic and Technological Considerations - The Asahi Process involves a complex series of chemical processing steps. Furthermore, the system has not been demonstrated on flue gas from coal-fired boilers, so workability in such applications is unproven. The process requires a large amount of mechanical equipment. There are six solid-liquid separation steps, six chemical reactors, two thermal decomposers, one crystallizer, and one dryer in the regeneration section. The required absorbers are larger than those used in conventional limestone desulfurization systems because of the high L/G and low gas velocity used. However, the equipment in the regeneration section is much smaller. Most of the equipment is polymer or glass-lined, but some equipment is 310 or 316 stainless steel.

Applicability - The process may be suitable for utility and industrial application. Decoupling may be somewhat difficult because of the reheat from the regeneration section, and the large storage volume required. It should have good load following capabilities, but turndown may decrease NO_x removal efficiency. The process is judged easily retrofittable if enough land is available. By-product gypsum and sodium sulfate will probably be landfilled because of limited marketability in the U.S.

Summary and Conclusions - This process was rated below average. Advantages for the process include simultaneous removal of NO_x and SO_2. Disadvantages include complexity, high energy requirements, large equipment requirements, and lack of development for coal-fired units. This process is not recommended for further consideration.

References - FA-149

ASARCO DIMETHYLANILINE PROCESS

Process/Subsystem Description - The Asarco process was developed to clean smelter gases. The gases are cooled, cleaned of particulates and sent to an absorption tower with 3 separate sections. In the first section, SO_2 is absorbed in dimethylaniline (DMA). The second section is irrigated with a dilute solution of sodium carbonate which reacts with residual SO_2 in the gas to form a sodium sulfite or bisulfite solution that improves overall SO_2 recovery. In the third section, DMA vapor is recovered from the gas stream by dilute sulfuric acid. The DMA is regenerated by steam stripping in a three section stripping tower. In the first section soluble DMA and SO_2 are removed from the aqueous phase from the absorption tower. DMA is regenerated and SO_2 released in the second section. The hot, concentrated SO_2 gas stream is cooled in the third section, and DMA is scrubbed from the gas stream with water. The SO_2 gas leaving the stripping tower is dried and liquefied.

Environmental and Energy Considerations - Removal efficiencies for SO_2 of up to 99% have been reported. Secondary pollution problems could be severe. The DMA must be completely recovered to prevent its release to the atmosphere. Also, a wastewater stream containing sodium sulfate is produced. There does not appear to be potential for removal of other pollutants. Energy requirements could be high; three different liquids must be circulated in the absorber, steam is required for regeneration, and gas reheat would probably be needed. Sodium carbonate, sulfuric acid and makeup dimethylaniline are the raw materials required.

Development Status - The process has been used to clean waste gases from small smelters (including a 45,000 cfm unit at Asarco's Tacoma copper smelter), but has not been tested on power plant flue gases. The process has not been integrated with SO_2 disposal. The absorber and stripper require the use of some technology that is not currently well defined. Scale-up problems should be minimal since commercial scale units have been constructed.

Economic and Technological Considerations - The need to completely recover the DMA to prevent expensive makeup requirements and environmental contamination makes the process extremely complex mechanically. A three stage absorber, with three separate liquor loops, and a three stage stripping tower are used to prevent DMA losses. Because dissolution of SO_2 in DMA liberates heat, The DMA must be cooled during its downward flow through the column in order to achieve efficient SO_2 absorption. Absorption and stripping chemistry is well understood; however, SO_2 conversion is chemically complex.

Applicability - Since the process has not been tested on a coal-fired boiler, the effect of fuel contaminants is unknown. Extremely efficient particulate removal prior to SO_2 removal appears to be necessary, however. The process may not be practical for utility or industrial boiler applications with low concentrations of SO_2 in the gas to be treated. Some use of special construction materials will probably be required. A stream of concentrated SO_2 (which is then liquefied) is produced as a by-product. Retrofits may be somewhat difficult because of the complex three stage absorber used. The absorption and stripping operations can not be decoupled. Industrial modularization appears possible.

Summary and Conclusions - The ASARCO DMA process rated as average in the evaluation of the wet regenerable processes. This rating is due primarily to raw material and reheat requirements and process equipment complexity. Advantages of this process over others in its class are not apparent. Disadvantages include an expensive absorbent, potentially severe secondary pollutant problems, and potentially high energy requirements. Although the process is not recommended for individual process evaluation, it should be considered in the general evaluation of absorption and steam stripping.

References - CA-327, HE-133

ASARCO SULFUR PLANT

Process/Subsystem Description - The ASARCO subsystem reduces SO_2 to sulfur catalytically using a methane based reducing gas. A minimum SO_2 content of 10 to 15 percent is required. Oxygen content cannot exceed 2 to 3 percent. In the primary reactor, the reaction occurs at 650°F with an organic heat transfer media used to remove the heat of reaction from the reactor. Other reactors in series are required with sulfur removal between reactors to obtain a conversion efficiency greater than 90%.

Environmental and Energy Considerations - This process has only been demonstrated using natural gas to produce the reducing gas. Because of the decreasing availability of natural gas, this process must be demonstrated using a coal based reducing gas. Offgas treatment for sulfur compounds would probably be required unless 99+ percent conversion of SO_2 could be demonstrated.

Development Status - A pilot plant with a 20 TPD of sulfur production capacity was operated in 1971 and 72. Boiler corrosion, catalyst decrepitation causing high pressure drop, and tube sheet warpage in the primary reactor due to poor heat transfer were major problems associated with the pilot plant operation.

Economic and Technological Considerations - This subsystem would have to be demonstrated using a coal based reducing gas. Energy requirements for producing the reducing gas would be high. This process uses commercial technology but is mechanically complex.

Applicability - This subsystem could be coupled with FGD systems producing an SO_2 product with low oxygen. Production of a reducing gas is required.

Summary and Conclusions - This subsystem is similar to the Allied Reduction process except that the H_2S produced is completely converted to sulfur in Claus type reactors. However, this process has not been demonstrated using a coal based reducing gas. Energy cost for production of the reducing gas would be high. Consequently, this process was not recommended for further evaluation.

References - HE-120

BERGBAU-FORSCHUNG

Process/Subsystem Description - The Bergbau-Forschung process adsorbs SO_2 on a moving bed of activated carbon at 200-300°F. The carbon pellets are removed to the regenerator where they are thermally regenerated at 1200°F by contact with hot sand in a reducing atmosphere. Off gas from the regeneration is 10-20% SO_2 and is suitable for sulfur or sulfuric acid production.

Environmental and Energy Considerations - SO_2 removal up to 99% has been claimed and NO_x removal of 40-60% has been reported. Stack gas reheat is not required for the process. However, a significant quantity of heat must be supplied for heating of the sand used in the carbon regeneration step. Solid wastes from the unit can be handled by the plant ash disposal system. The major raw material, Bergbau char, is produced only in Germany.

Development Status - The BF Process has been thoroughly and successfully tested at the bench (200 scfm), pilot (1750 scfm), and prototype (88,000 SCFM) level in West Germany. The pilot and prototype testing were on coal-fired utility boilers. Research has also been done on the char adsorbent. A BAMAG modified-Claus unit was added to the prototype in 1975 to produce sulfur as the by-product. The BAMAG unit has only operated for limited periods due to operating problems. Testing at the prototype which is sponsored by the West German government is scheduled to end in late 1978.

Foster Wheeler (a licensee of the BF Process) built a prototype unit in the U.S. which included FW's proprietary RESOX process to produce sulfur. This plant experienced only limited success due primarily to operational problems caused by FW in efforts to reduce costs and is not presently operational.

Economic and Technological Considerations - Although this process is quite complex mechanically, it is rather simple chemically. Spontaneous combustion in the carbon beds and solids handling throughout the system are continuing problems. The limited availability of adsorbent char may also affect process economics.

Applicability - The overall mechanical complexity of this process affects its applicability to both utility and industrial users in the areas of turndown, retrofitability, and modularization. However, the process can be decoupled and produces a marketable product.

Summary and Conclusions - The Bergbau-Forschung process scored well compared to other dry processes. Advantages of the process include no requirement for stack gas reheat, chemical simplicity, a potential reduction in particulate removal requirements prior to SO_2 removal (removed in char bed), potential for NO_x removal and low makeup water requirements. Disadvantages include the mechanical complexity involved with the large quantities of solids that are being transported and high maintenance costs. Its leading status in the genre of carbon adsorption processes merit its further evaluation.

References - BI-072, BI-073, BI-031, DR-850, HA-352, MU-058, SL-070, ST-292, ST-369

BUREAU OF MINES MANGANESE DIOXIDE PROCESS

Process/Subsystem Description - Of the potential sorbents for use in dry flue gas desulfurization, MnO_2 shows the most rapid adsorption rate for SO_2. The first step in the BOM Process is adsorption of the SO_2 on MnO_2 to yield $MnSO_4$. The adsorbent is regenerated by reactivating $MnSO_4$ with NaOH, which precipitates MnO_2 and produces Na_2SO_4 solution. The Na_2SO_4 solution is electrolytically converted to NaOH and H_2SO_4. The NaOH is reused, and the H_2SO_4 is a by-product.

Environmental and Energy Considerations - The process should be capable of greater than 90% SO_2 removal, and there appears to be potential for removal of NO_x by analogy with the Shell/UOP copper oxide process (ammonia injection). A marketable by-product (weak acid) is produced, but the potential for manganese losses to the environment poses a serious problem. No reheat or reducing gas is needed, but the electrolysis step is a high energy user. The raw materials (MnO_2 and NaOH) are recycled, but even small MnO_2 losses will be expensive.

Development Status - The dry MnO_2 process was tested on a bench scale in the 1950's, but there seems to have been no work since that time. There are no indications that the process was integrated on any scale. The system would require considerable equipment development, so scale-up would be difficult.

Economic and Technological Considerations - This process is chemically complex involving a gas-solid reaction, a dissolution/precipitation reaction, and an electrolysis step. The process requires a variety of mechanical equipment to perform solids handling, pumping and handling of three liquid streams, filtration, and electrolytic decomposition. The process would present major difficulties from both a process control and a maintenance standpoint.

Applicability - For either industrial or utility applications, the dry MnO_2 process should be suitable for retrofit applications. The process can only partially be decoupled, without installing large surge capacity at several points. The weak sulfuric acid produced has only limited marketability.

Summary and Conclusions - The Bureau of Mines MnO_2 Process rates very poor in terms of environmental and energy impacts, development status, economic and technological considerations, and applicability. It is not recommended for further evaluation.

Reference - SL-070

CALCIUM SULFATE REGENERATION

Process/Subsystem Description - Several processes that involve thermal decomposition of calcium sulfate to lime or limestone have been investigated. Limestone regeneration processes such as the Pullman Kellogg Kel-S Process and the Ontaria Hydro process typically reduce calcium sulfate to CaS at high temperature and use the reaction of the sulfide or a hydrosulfide with CO_2 and water to produce calcium carbonate and H_2S. Lime regeneration processes generally involve reducing calcium sulfate with CO and hydrogen to produce calcium oxide, CO_2, water, and SO_2. The H_2S- or SO_2-rich streams produced have to be treated for sulfur or sulfuric acid production by conventional methods.

Environmental and Energy Considerations - Due to the stability of calcium sulfate and sulfite, the energy requirements to decompose these by-products will be much higher than those for many other SO_2 sorbents. Regeneration to lime is even more energy intensive than to limestone because more heat is required to reduce the calcium species to CaO than to the intermediate CaS in the limestone scheme.

Development Status - The regeneration schemes mentioned have not been developed past the pilot plant scale. However, a process for the recovery of sulfur from gypsum with a limestone by-product was used in Europe in the latter part of the last century.

Economic and Technological Considerations - The large fuel and reducing agent consumption and the high operating temperatures, which necessitate expensive materials of construction, make it unlikely that a regenerable lime or limestone process could compete with other regenerable processes.

Applicability - While these systems could easily be decoupled from a scrubbing system, making them applicable to most retrofit installations, they offer no advantage over other less expensive regenerable FGD systems.

Summary and Conclusions - $CaSO_4$ regeneration subsystems were developed to make lime-limestone scrubbing processes regenerable. However, because of the high energy and capital requirements for the regeneration facilities, it is unlikely that these subsystems can compete against other regenerable processes. Consequently, these subsystems were not recommended for further evaluation.

References - OT-R-51

CALLERY CHEMICAL CATALYTIC OXIDATION

Process/Subsystem Description - The Callery Chemical Process has some similarity to other catalytic oxidation processes such as Cat-Ox, but it includes a process modification which yields a more concentrated sulfuric acid product. The initial step is passage of the hot, fly ash-free flue gases through a converter bed of V_2O_5, where SO_2 is oxidized to SO_3. Instead of cooling this gas stream and absorbing the SO_3 in dilute H_2SO_4 as in Cat-Ox, the SO_3 is absorbed in Na_2SO_4 at 500-600°F to form sodium pyrosulfate ($Na_2S_2O_7$). The pyrosulfate is separated and heated to 930-1020°F, where it decomposes, yielding Na_2SO_4 and a 6% SO_3 gas mixture. This SO_3 can be absorbed in water to yield a concentrated H_2SO_4 product.

Environmental and Energy Considerations - Because the initial SO_2 oxidation step is the principal determinant of the removal efficiency and this step is the same as for Cat-Ox, the Callery Chemical Process would be expected to show the same efficiency as Cat-Ox or about 90%. Excellent fly ash removal ahead of the converter is mandatory for successful operation. Other than fly ash disposal, no secondary pollution problems are foreseen. The process requires no reheat or reducing gas, but the pyrosulfate decomposition step requires substantial energy input. The pressure drop across the system is probably moderately high.

Development Status - Callery Chemical investigated the process on a laboratory scale, but apparently no pilot plant work was undertaken.

Economic and Technological Considerations - This process is more complex than direct conversion to acid as in Cat-Ox, from both a chemical and mechanical standpoint. Decomposition of SO_3 to SO_2 at high temperatures in the regenerator means that about 12% of the SO_2 must be recycled back to the converter resulting in a large efficiency loss. Although it produces a more concentrated acid product, the capital and energy costs seem greater than those for integrated Cat-Ox.

Applicability - The retrofit potential is poor since the flue gases from existing boilers would require a great deal of reheat. The process can be decoupled after absorption with intermediate storage for Na_2SO_4. However, hot solids storage facilities and/or thermal losses may prohibit such application. Good turndown capability can be accomplished if Na_2SO_4 storage is provided.

The by-product (sulfuric acid) is more concentrated than that produced by Cat-Ox, so it should be marketable.

Summary and Conclusions - The Callery Chemical Process has not been developed beyond the bench scale and it is chemically and mechanically complex, so scale-up would probably be difficult. In addition, it is rated low in terms of applicability and energy use. The process is not recommended for further evaluation.

References - FA-149.

CALSOX

Process/Subsystem Description - SO_2 is absorbed in an amine sulfite solution. Spent scrubber solution is regenerated at a pH of 10 with lime to produce $CaSO_3/CaSO_4$ solids and aqueous free amine. Scrubber feed solution is softened by reaction with the scrubber product to precipitate $CaSO_3$ solids which are separated before scrubbing.

Environmental and Energy Considerations - Good SO_2 removal (>90%) should be possible. The process does not appear to have potential for multipollutant removal. Serious secondary pollution problems could result from disposal of the waste solids. Use of a nonvolatile amine such as ethanolamine prevents the fume formation that results from ammonia scrubbing. Energy requirements are comparable to these for other scrubber systems; reheat will be required and L/G and pressure drop should be relatively low. Lime and makeup ethanolamine are required as raw materials.

Development Status - This process was tested by Monsanto in 1972 at a 2000 cfm coal-fired pilot plant, but is not currently offered. The process has been integrated and does use current technology. Relatively minor scale-up problems may be experienced.

Applicability - This process appears to be generally applicable for utility or industrial use. It can be turned down, retrofitted, and modularized. Process sections can be decoupled. Applicability is limited by the need to dispose of large quantities of waste products. The process is not applicable for cleaning gas from fuels with a high concentration of chlorides without a separate chloride removal system.

Summary and Conclusions - This process scored about average compared to other throwaway processes. It scored slightly below average in Environmental and Energy Consideration and above average in Economic and Technological Considerations. It is not as well developed as some of the other throwaway processes. Regeneration is more complex for Calsox than for sodium/lime double alkali, but the Calsox process is suitable at any level of oxidation. Lime must be used for regeneration and some expensive amine makeup is required. This process is not recommended for further consideration.

References - BA-225

CARBON ADSORPTION/INERT GAS STRIPPING (REINLUFT/CHEMIEBAU, SUMITOMO)

Process/Subsystem Description - The Reinluft/Chemiebau and Sumitomo processes are very similar carbon adsorption processes. Adsorption is accomplished in downflow countercurrent adsorbers in the Reinluft/Chemiebau process and in cross-flow adsorbers in the Sumitomo process. The carbon with SO_2 adsorbed is then taken to a desorber where it is stripped with an inert gas at 750°F. The SO_2 rich gas is passed through an electrostatic precipitator and then to sulfuric acid production.

Environmental and Energy Considerations - The processes have shown SO_2 removals of 80-90% and have some potential for NO_x removal. Secondary pollutant problems are present only in the carbon fines that must be disposed of. The processes do not require stack gas reheat or reducing gas. Pressure drop through the adsorber is fairly large and raw material consumption in the form of carbon is a significant process problem. Energy requirements for the inert stripping gas are also high.

Development Status - The Reinluft/Chemiebau and Sumitomo processes have been demonstrated in plants as large as 70 MW and are thus fairly well developed. These plants have been operated in an integrated mode. However, they have not been applied to coal-fired power plants in this integrated mode. Scale-up of the adsorbtion step in the process is a significant problem. Further development of the processes does not seem to be occurring at this time.

Economic and Technological Considerations - The processes may be regarded as fairly simple from a chemical standpoint. However, they are very complex mechanically. A major problem has been hot spots in the carbon bed. The major economic problem is the large requirement for carbon to replace that lost through attrition.

Applicability - The processes would seem to have a fair opportunity for utility and industrial retrofit. Operation of the beds in a turndown or decoupled mode would be difficult but could be accomplished.

Summary and Conclusions - The Reinluft/Chemiebau and Sumitomo processes appear to be undergoing no further development at this time and are not recommended for further consideration. The problems of carbon attrition and mechanical complexity appear to be the major impediments to further development.

References - SL-070

CARBON ADSORPTION-THROWAWAY

(HITACHI, LURGI SULFACID)

Process/Subsystem Description - The common element in the Lurgi Sulfacid and Hitachi processes is the washing of H_2SO_4 off of activated carbon. In the Lurgi process, SO_2 is concurrently contacted with a weak sulfuric acid solution and then contacted with a carbon adsorbtion bed which is continually washed with water. The flue gas is then reheated and sent to the stack. In the Hitachi process, the SO_2 is adsorbed in a fixed dry bed of activated carbon and then the carbon is washed in a batch mode. Thus, the concepts of the two processes are similar, but the Sulfacid process is operated in a continuous mode and the Hitachi process in a batch mode. Both of these processes produce a 20 to 30% sulfuric acid solution. This acid may be concentrated, utilized nearby as a weak acid or neutralized with limestone to produce gypsum.

Environmental and Energy Considerations - The processes have been demonstrated to reduce SO_2 emission by 90%. There is some potential for NO_x removal through ammonia addition. Disposal of carbon fines can be a minor secondary pollutant problem. If the acid is neutralized to produce gypsum, other secondary pollution problems could result from disposal of the gypsum. A reducing gas is not required and stack gas reheat is required only in the Sulfacid process. Activated carbon is a major raw material cost although limestone is utilized in significant quantities in the throwaway version of the process.

Development Status - The Sulfacid process has been developed and run in an integrated fashion at a small scale (1 MW). Attempts to adapt the process to larger scale have not proceeded. The Hitachi process has been run at the 150 MW level but further application has not come about. The Japanese seem to feel that other FGD alternatives are more viable. The process utilizes current technology in most process areas, but also uses some novel technology. Minor scale-up problems may be encountered.

Economic and Technological Considerations -The processes can be regarded as fairly simple chemically, but relatively complex mechanically. The major problem is waste disposal. The dilute sulfuric acid must have a readily accessible market since production of concentrated sulfuric acid is expensive and gypsum does not have a ready market in the United States.

Applicability - The systems could be retrofitted to existing utility or industrial boilers providing sufficient space is available. The processes could be turned down and could be decoupled. Operation of the batch system could be controlled by intermediate tankage for the dilute sulfuric acid.

Summary and Conclusions - The developers of the processes have not further developed or installed them on large boilers. This seems to be principally due to problems with disposal of the weak sulfuric acid. Concentration is not easy and neutralization to gypsum is not satisfactory except as landfill in the United States. The processes seem to have no large advantages over others under development and consequently are not recommended for further evaluation.

References - CA-327, SL-070

CHISSO ENGINEERING PROCESS

Process/Subsystem Description - The Chisso Engineering Process uses an $(NH_4)_2SO_3$ solution containing a proprietary iron chelate to absorb SO_2 and NO_x from flue gas. A prescrubber removes particulates and chlorides before the gas enters the absorber. The clean flue gas discharged from the top of the tower is demisted, reheated, and discharged through the stack. A portion of the sorbent is processed in a series of chemical processing steps to recover the catalyst, regenerate the sorbent, and produce ammonium sulfate.

Environmental and Energy Considerations - Bench-scale testing of an oil-fired unit showed 95% SO_2 removal and 80% NO_x removal. The prescrubber also removes particulates and chlorides. Disposal of solid by-products may prove to be an environmental problem if they cannot be marketed. A sulfitic plume from the absorber has been cited as a major drawback to this process and design modifications of the absorber have been suggested to correct the problem. Flue gas reheat is necessary to insure plume buoyancy. A requirement for reducing gas is not indicated. High L/G ratios (65-100 gal/Mcf) indicate the potential for high energy requirements associated with pumping and pressure drop. Temperatures in the thermal decomposer are less severe than those encountered in other processes of this type. Raw materials required are liquid ammonia, sulfuric acid, and makeup catalyst.

Development Status - An integrated bench-scale unit treating 177 scfm has been tested on flue gas from an oil-fired boiler. The process has not been tested on coal-fired flue gas so that scale-up poses a potential problem. Commercialized technology is used throughout the process.

Economic and Technological Considerations - The Chisso Engineering Process incorporates a complex series of chemical reactions; although, it is somewhat less complex than the Asahi Chemical Process. The workability of the chemical processing methods is questionable because it has not been demonstrated on coal generated flue gas. Although the Chisso Process is less complex than some of the other NO_x/SO_x removal processes overall, many pieces of equipment are still required in the regeneration section: three centrifuges, two crystallizers, one thermal decomposer, one oxidizing tower, and five tanks or reactors. The absorption system utilizes four large tray towers. There are relatively few pieces of solids handling equipment required.

Applicability - This process may be suitable for utility and industrial applications. Decoupling would require large volumes for intermediate storage. Load following capacity should be good because any combination of the four absorbers can be shut down. The process should be easy to retrofit if enough land is available. The ammonium sulfate by-product may not be of high enough quality to compete in the fertilizer market. A process modification has been suggested in which the IFP Process is incorporated to produce an elemental sulfur by-product stream. This modification would add complexity to the process plus the requirement for reducing gas.

Summary and Conclusions - The Chisso process rated below average. An advantage for the process is that NO_x and SO_2 are removed simultaneously. Disadvantages include complexity, large equipment requirements, lack of development for coal-fired units, the need for reheat and high energy requirements. This process is not recommended for further consideration.

References - FA-149

CHIYODA THOROUGHBRED 101

Process/Subsystem Description - The Chiyoda Thoroughbred 101 Process utilized a weak sulfuric acid stream at high liquid/gas (L/G) ratios to scrub SO_2 from flue gas. The flue gas is adiabatically saturated to 120°F - 140°F in a venturi prescrubber. The flue gas is countercurrently contacted with a water (weak sulfuric acid) solution in a packed tower with sufficient L/G that 90% of SO_2 is removed. The stack gas goes to a mist eliminator for entrained liquid removal, is reheated and vented. The liquid stream goes to an oxidizer where it is run countercurrently to air to oxidize the H_2SO_3 to H_2SO_4. Iron pellets in the liquid stream catalyze this oxidation. The oxidized liquor is transferred to a crystallizer where limestone is added. The resulting calcium sulfate slurry is clarified, with the gypsum solid utilized as landfill or for production of wallboard and the water returned to the absorber.

Environmental and Energy Considerations - SO_2 removal of 90% has been achieved. The process may have potential for removing other pollutants. Secondary pollution problems could result from disposal of the gypsum. Energy requirements are somewhat higher than those for the double alkali process. Gas reheat is required, and the L/G is very high. Limestone and catalyst ($Fe_2(SO_4)_3$) are required as raw materials.

Development Status - This process has been demonstrated commercially on oil-fired boilers in Japan in 13 commercial units up to 250 Mw, and at a 20 Mw coal-fired prototype in the U.S. The process has been fully integrated. It uses current technology, but some scale-up problems may be experienced.

Economic and Technological Considerations - This process has about the same degree of chemical complexity as the sodium double alkali process, but is more complex mechanically. The use of stainless scrubber internals has required solution purge and prescrubbing to avoid chloride buildup.

Applicability - The applicability of this process for utility and industrial use does not appear to be as good as that for other throwaway processes. The process can be turned down and modularized, but retrofits would be difficult because of the large scrubber required. Decoupling the process steps may also be difficult. Applicability is further limited by the need to sell or dispose of large quantities of gypsum which, although easier to dispose of than sludge, nevertheless requires land for disposal if the product cannot be sold. The process is more attractive for cleaning flue gas with low concentrations of chloride and SO_2.

Summary and Conclusions - This process scored above average compared to other throwaway processes. It is well developed and scored above average in Environmental and Energy Considerations, but it scored lower in applicability than other throwaway processes because of the difficulty in retrofitting it. Extremely high L/G ratios are required to achieve adequate SO_2 removal. In addition, the process is more sensitive to chlorides than some other throwaway processes. It is not recommended for further evaluation principally due to the fact that Chiyoda considers the CT-121 process to be an improvement over the CT-101.

References - AN-056, DA-271, NO-054, SL-070.

CHIYODA THOROUGHBRED 102

Process/Subsystem Description - This process uses ozone for oxidation of nitric oxide to nitrogen dioxide. Sulfur dioxide and nitrogen dioxide are then absorbed by a weak sulfuric acid solution containing ferric sulfate. Limestone is added to the acid solution to form by-product gypsum and the remaining solution is treated biologically to reduce nitrates to molecular nitrogen. Particulates and chlorides are removed from flue gas in a prescrubber. The gas is then treated with ozone, contacted with sorbent solution in the absorber, reheated, and exhausted through the stack. The Chiyoda Thoroughbred 102 Process was developed by adding the ozone injection and biological treatment steps to the Thoroughbred 101 flue gas desulfurization process.

Environmental and Energy Considerations - Pilot plant tests have achieved 90-98% SO_2 removal and 80% NO_x removal. Particulates and chlorides are also removed. The gypsum is expected to be landfilled and could create an environmental problem. Treatment of the nitrate wastes will be difficult for large installations. The ozone and acid streams pose a potential hazard to workers. Reheat of the flue gas is required to insure plume buoyancy, and high L/G ratios are required. Reducing gas is not required. Ozone is required and generation of ozone is very energy intensive. The major raw materials required are limestone and ferric sulfate catalyst.

Development Status - This process has not been tested on flue gas from a coal-fired unit. Pilot plant scale testing has been performed on flue gas from an oil-fired boiler. The Thoroughbred 101 Process from which this process evolved is being tested on a prototype (20 Mw) coal-fired boiler. The process is integrated and utilizes commercially available technology. There are some potential scale-up problems stemming from the fact that the process has not been demonstrated on flue gas from coal. However, experience gained in applying the Thoroughbred 101 Process to coal-fired units and scaling it up should provide valuable information for solution of these problems.

Economic and Technological Considerations - The chemical and mechanical complexity involved in this process is less than many of the other NO_x/SO_x removal processes. A relatively complex biological treatment system is required for treatment of the nitrate waste.

Applicability - The process may be useful for industrial and utility installations. It will be expensive to decouple, however, because of the large volumes of liquid required for absorption. It is judged easy to retrofit. Load following capabilities are also expected to be good. The by-product gypsum will probably have to be landfilled. Operation of a biological water treatment system is an unfamiliar problem for utilities and could hamper utility applicability.

Summary and Conclusions - This process was rated below average. It has some design and development problems which will have to be solved although the Thoroughbred 101 Process development provides valuable information. The process has high energy requirements, requires flue gas reheat, and utilizes a unique method of waste treatment. It does remove SO_2 and NO_x simultaneously. The process is not recommended for further consideration.

References - AN-056, DA-271, FA-149, NO-054, SL-070.

CHIYODA THOROUGHBRED 121

Process/Subsystem Description - The Chiyoda Thoroughbred 121 (CT-121) process uses a slurry scrubbing with forced oxidation in the scrubber. The hot flue gases are cooled in a water prescrubber before being sparged into a limestone slurry maintained in the bottom of the SO_2 scrubber. The SO_2 is absorbed by the limestone slurry in the scrubber. Air which is also sparged through the limestone slurry, oxidizes the calcium sulfite formed to gypsum. The gypsum settles to the bottom of the scrubber where it is pumped to centrifuges for gypsum recovery. The liquid from the centrifuges goes to a limestone slurry tank where it is mixed with limestone makeup and limestone slurry from the scrubber. The resulting limestone slurry is pumped to the scrubber. The scrubbed flue gas leaves the top of the scrubber, flows through a mist eliminator and is reheated before venting. The absorption, oxidation, and crystallization processes are combined into one reactor vessel.

Environmental and Energy Requirements - This process should be capable of good SO_2 (>90%) removal, but does not appear to be capable of multipollutant removal. Secondary pollution problems could result from disposal of the gypsum. Energy requirements for pump around are low because of the simplified plant design, but gas pressure drop is somewhat higher than usual. Flue gas reheat is required. Limestone is the only raw material required.

Development Status - This process has been tested at the bench scale and pilot plant level since 1975, and a conceptual design for a 125,000 scfm plant has been completed. The process has been fully integrated. Technology that is not currently commercial is used in parts of the process. Some scale-up problems may be experienced.

Economic and Technological Considerations - This process is less complex chemically and mechanically than the sodium double alkali process. The scrubber is more complex than those in many other throwaway processes, but the simplified overall plant design has the potential to minimize capital and operating costs.

Applicability - This process appears to be generally applicable for utility or industrial use. It can be turned down and modularized, but industrial retrofits may be somewhat difficult. Applicability is somewhat limited by the need to dispose of large quantities of gypsum.

Summary and Conclusions - This process scored above average compared to other throwaway processes. It is less developed than some of the other throwaway processes, but is relatively simple and scored well in Environmental and Energy Considerations because of its potential for performance growth. The scrubber is more complicated than that used for some limestone slurry scrubbing processes and it is more difficult to achieve good SO_2 removal and limestone utilization with this process than with the simple limestone slurry process. Because of the simplified overall plant design, however, the CT-121 process has the potential for lower capital and operating costs. This process is recommended for further consideration principally because of its potential in these areas.

References - CH-398

CITRATE DOUBLE-LOOP REGENERATION

Process/Subsystem Description - The Citrate double-loop regeneration is a modification to the Citrate process. The liquor out of the absorber is regenerated in two steps or loops rather than the conventional one loop for the Citrate process. In the first loop, the absorbed SO_2 is reacted with about 25 percent of the stoichiometric amount of H_2S gas (required for reduction to sulfur) to convert the SO_2 to thiosulfate and polythionates without forming elemental sulfur. Most of this solution is recycled to the absorber. A slipstream from the first loop is reacted with greater than 75 percent of the stoichiometric H_2S to convert the thiosulfate and polythionates to elemental sulfur. The sulfur slurry formed in the second loop should be sufficiently concentrated to melt and separate without treatment by a flotation step. The solution from the second loop is recycled to the absorber.

Environmental and Energy Considerations - Although double-loop regeneration is conceptual, the environmental and energy requirements for the Citrate process with this modification should not change significantly from those for the Citrate process with single-loop regeneration.

Development Status - Double-loop regeneration is conceptual. The Citrate process is to be demonstrated at the 60 Mw level in the near future. The effort necessary to develop double-loop regeneration will be reduced since it is a modification to a demonstrated process. The chemistry of the basic Citrate process would be changed significantly for double-loop regeneration and the resulting effect on the basic design is unknown at this time.

Economic and Technological Considerations - Double-loop regeneration offers two potential economic advantages: 1) elimination of the flotation equipment used in sulfur separation, and 2) reduced costs for decoupling since tankage could be placed in the second loop which treats only a slipstream of the absorber solution.

Applicability - Applicability relative to the conventional Citrate process should be improved due to the reduced costs of decoupling and the elimination of the flotation processing step.

Summary and Conclusions - The double loop alternative to the Citrate process offers potential advantages over the basic Citrate process. It will be further considered in the Citrate process summary paper.

Reference - RO-333

CLAUS PROCESS

Process/Subsystem Description - The Claus process is a catalytic oxidation process for recovering elemental sulfur from gas streams containing at least 10 to 15% H_2S, such as the acid gases stripped from regenerable liquids used in some FGD processes. The feed stream is either partially combusted or one third of the stream is split off for complete combustion in order to achieve a 2:1 ratio of $H_2S:SO_2$ in the reactor feed. Because of the exothermic nature of the reversible reaction of H_2S and SO_2 to form elemental sulfur, thermal constraints limit the amount of conversion which can be achieved in one reactor. Consequently high conversions typically require a series of convertors and sulfur condensers.

Environmental and Energy Considerations - Equilibrium considerations limit the process from being a final sulfur control process; consequently, a tail gas cleanup process is required. Spent catalyst, with possible ammonia, carbon, and/or sulfur compounds present, can present a solid waste disposal problem. The process is a producer of waste heat steam.

Development Status - This process is commercially available.

Economic and Technological Considerations - The process requires a feed stream containing at least 10-15% H_2S to be economical. Corrosion, especially in the sulfur condensers, often necessitates the use of expensive materials of construction.

Applicability - Hydrocarbons, CO_2, trace elements and high concentrations of ammonia (>3%) in the feed gas can cause operating problems such as catalyst deactivation, equipment fouling, and formation of undesired by-products. These interferences may limit the use of the Claus process with some regenerable FGD systems.

Summary and Conclusions - This process has been in commercial use for years but requires low levels of hydrocarbons, trace elements and ammonia in the H_2S feed stream which may limit its use with some FGD systems. In addition, for use by some FGD systems, conversion of SO_2 to H_2S is required which causes high fuel and reducing gas consumption. Consequently, this process was not recommended for further evaluation.

References - BE-373, DR-066, GA-135, GO-107, HO-174, PE-142, RI-114

ClO_2 PROCESS

Process/Subsystem Description - An aqueous solution of ClO_2, detergent, and possibly additional alkali or an organic solvent is injected into the flue gas by an atomizer. The precise mechanism of SO_2 removal is not understood, but it is believed that the ClO_2 oxidizes the SO_2 to SO_3 which then forms sulfuric acid upon contact with moisture. The sulfuric acid is presumed to be converted to sulfate or other material which is recovered or passed on into the atomsphere.

Environmental and Energy Considerations - SO_2 removal efficiencies of 75-90% are possible by varying the amount of ClO_2 used. No other pollutants appear to be removed, and secondary pollution problems could be severe. The sulfur is believed to be converted to sulfates that may be collected by the electrostatic precipitator. The fate of the chlorine is unknown. Energy requirements should be quite low, but some reheat may be required. Several different raw materials may be required. These include ClO_2, detergent, and possibly some other alkaline material (such as an ammonium or alkali metal hydroxides or carbonate) or an organic solvent (such as one of the lower alkyl or polyhydric alcohols).

Development Status - The process has been tested on the bench scale using conventional atomizers for injection of the ClO_2 solution. The process has not been integrated. Serious scale-up problems may be encountered.

Economic and Technological Considerations - This process is more complex, chemically and mechanically, than the double alkali process. The chemistry of the process is not understood, and the effect of the injection on the flue gas duct work is unknown. Also, the proposed option of releasing sulfates and possibly chlorine directly into the atmosphere is unacceptable.

Applicability - Applicability of this process for utility and industrial applications appears to be quite poor. It can be turned down and modularized, but retrofits may be unfeasible because of the possible corrosive effect of the injection on the flue gas duct work. The need to dispose of the waste products (the form of which is not precisely known) in an environmentally acceptable manner also limits applicability.

Summary and Conclusions - This process scored very low compared to other throwaway processes. It scored below average in Environmental and Energy considerations because of its low SO_2 removal and serious secondary pollution problems. In addition, it is relatively complex, undeveloped, and has poor applicability. The major disadvantages of the process are its low state of development; expensive raw materials; and formation of uncertain, potentially environmentally significant products. It is not recommended for further evaluation.

Reference - SH-344

COCURRENT SCRUBBING

Process/Subsystem Description - Cocurrent scrubbing is a process alternative for wet scrubbing systems. The basic concept of cocurrent scrubbing is a high-velocity scrubber resulting in massive entrainment followed by a change-of-gas direction and a properly designed mist eliminator. The actual scrubber may use sprays, packing, or venturi principles for gas/liquid contact.

Environmental and Energy Considerations - The disadvantage of cocurrent scrubbing is the reduced mass transfer driving forces due to cocurrent gas and liquid flow. However, high SO_2 removal can be obtained by increasing the L/G. Testing at a 1 MW pilot plant showed that the cocurrent scrubber was capable of achieving 90 percent removal using lime or limestone as an absorbent. This test was in a scrubber with internal packing. An advantage to the process is that the liquid flow imparts additional energy to the gas so that only a small pressure drop is realized across the scrubber. Overall, the cocurrent scrubber may consume less energy than a countercurrent scrubber because the energy saved by the low pressure drop should be greater than the additional energy needed for the larger liquid pumping requirement.

Development Status - The concept has been widely used in commercial FGD systems in Japan by Mitsubishi Heavy Industries. In the U.S., TVA has performed pilot testing of a cocurrent scrubber on a 1 MW pilot unit.

Economic and Technological Considerations - The cocurrent scrubber concept is very simple mechanically. Higher gas velocities through the scrubber are possible; therefore, smaller diameter absorbers may be used. Since spray towers are generally designed for length to diameter (L/D) ratios of about 2 for good gas distribution, cocurrent operations are attractive from a liquid pumping height standpoint. In addition, the cocurrent scrubber concept may reduce the effect of plugged nozzles on gas distribution. In countercurrent designs the gas will tend to flow where the pressure drop is lowest (i.e., in the area of a plugged nozzle) which results in reduced mass transfer. However, in the cocurrent scrubber, the liquid flow imparts additional energy to the gas so gas will not tend to flow toward plugged nozzles. Instead, the gas flow should be higher in regions where the liquid flow is higher.

Applicability - The scrubber should follow load variations well and should retrofit well since it is smaller than a countercurrent scrubber. The cocurrent scrubber can be modularized very easily.

Summary and Conclusions - Cocurrent scrubbing is presently being used on a commercial level in Japan. Since poor gas distribution is a major concern, advantages in the cocurrent spray tower design, which include better gas distribution and reduced capital and operating costs, could more than offset any disadvantage of reduced mass transfer driving forces due to cocurrent gas and liquor flow. Cocurrent scrubbing will be further addressed as an option in lime/limestone scrubbing.

References - HO-395.

CONSOL PROCESS

Process/Subsystem Description - Flue gas is scrubbed in a packed tower with an aqueous solution containing various potassium salts. The actual removal of SO_2 occurs by reaction with carbonates in the feed solution. Sulfites are reduced to the thiosulfate with KAH as a reducing agent in a reaction drum in the scrubber circuit. The thiosulfate formed is noncatalytically reduced with a carbon monoxide-rich gas at elevated temperature and pressure. The H_2S released is selectively removed by scrubbing with a polar organic solvent and fed to a Claus plant for conversion to sulfur. Sulfate formation is low, but sulfates that are formed are removed as K_2SO_4 and sold.

Environmental and Energy Consideration - The Consol process is capable of SO_2 removal efficiencies of 99% but does not appear to have potential for multipollutant removal. There should be no solid or liquid waste streams requiring disposal. A small solid waste stream of K_2SO_4 is produced, but can be sold for use in the fertilizer industry. There is a potential for H_2S emission in the stack gas, however, if KHS enters the scrubber. The process has a low L/G and a pressure drop of around 14 to 15 inches of water. A CO reducing gas (produced by the partial oxidation of fuel oil) will be required. The stack gas must be reheated from saturation. Raw materials required are KOH for potassium makeup, oxygen and fuel oil for CO production, and Selexol (an organic solvent) to absorb H_2S.

Development Status - The absorption process was tested at a 1000 acfm (0.35 MW) oil-fired pilot plant at the Research Division of Consolidation Coal Company and of a 30,000 acfm (7 MW) coal-fired pilot plant at the Cromby Power Plant of Philadelphia Electric Company. A regeneration unit was integrated with the absorption unit at the 0.35 MW plant, but auxiliary processes such as partial oxidation (to produce CO), H_2S removal, and Claus technology have not been integrated. Conoco Coal Development Company considers these auxiliary processes to be commercially available. No serious scale-up problems should be encountered in the absorption section, but scale-up of the regeneration process will be more difficult. Current technology is used in some, but not all, process sections.

Economic and Technological Considerations - The process is very complex with many unit operations that must be integrated. Achieving proper agitation in the regeneration step (where mass transfer of CO from gas to liquid is rate limiting) may be difficult. Regeneration is both chemically and mechanically complex. Loss of sorbent must be kept to a minimum because of the high cost of makeup potassium. Special construction materials, such as rubber lined carbon steel, 316 stainless steel, or fiberglass reinforced pipe may be required for process equipment.

Applicability - Sulfur (produced from H_2S in a Claus unit) is the principal by-product from the process. A small amount of K_2SO_4 will also be produced, and sold for fertilizer manufacture. The process should be relatively easy to retrofit; the absorption and regeneration sections can be decoupled easily. Turndown ability and industrial modularization should also be easy.

Summary and Conclusions - The Consol process rated average in the evaluation of the wet regenerable processes. This was primarily because development work has been limited and the process is both chemically and physically complex. These disadvantages, along with the process' need for a reducing gas should eliminate this process from further consideration.

References - MC-303, SL-070, ST-504

COPPER OXIDE ADSORPTION
(SHELL, ESSO B&W, BUREAU OF MINES)

Process/Subsystem Description - In the CuO adsorption processes, SO_2 is removed by adsorption and reaction to $CuSO_4$ on an activated alumina-CuO substrate at 700°F. The adsorbent is regenerated in a batch mode by hydrogen at 700°F to produce concentrated (>15%) SO_2. The three processes involved are differentiated by reactor design. Shell uses cycling, fixed bed reactors with open passageways to avoid fly ash plugging. Esso/B&W uses cycling, fixed bed reactors. USBM uses fluidized bed reactors. In existing plants flue gas would be reheated to 700°F by cross-exchange and direct-firing of clean fuels. New plants could take gas before the air preheater through a hot ESP. Ammonia can be injected to give simultaneous reduction of NO_x to N_2.

Environmental and Energy Considerations - SO_2 removals of greater than 90 percent can be achieved. 80 percent NO_x reduction can be achieved by 1 mole NH_3/mole NO_x. The regeneration reaction produces a large amount of wastewater and disposal or recycle of this water has not been finalized at the time. Some steam could be required for reactor flushing and other applications. Reheat is required to get 700°F in retrofit applications. The process is penalized by high H_2 requirements.

Development Status - Shell has gone through several phases of testing but a completely integrated unit applied to a large coal-fired boiler has yet to be built. A 600 scfm pilot plant was constructed in the early 1970's and operated successfully. A large oil-fired unit (75,000 scfm) was operated successfully in Japan that confirmed design and scale-up assumptions. A unit has also been tested at 1,200 scfm on a utility boiler at Tampa Electric's Big Bend Station to answer questions about pressure drop, dust loading, and system stability. The process is offered in the United States by UOP.

Economic and Technological Considerations - The major technological impediment to commercialization is the duct work and reliable switching valves required for cycling operations. Residual fly ash can potentially plug or deactivate the adsorbent. Although the process is relatively simple from a chemical standpoint, the mechanical complexity is high.

Applicability - The process suffers in application to both utility and industrial boilers because of its difficulty in decoupling and retrofitability. Retrofit difficulties are due mainly to requirements for heating gas to the temperature required for adsorption (700°F).

Summary and Conclusions - The Copper Oxide process was rated about average compared to other dry FGD systems being evaluated. Advantages of the copper oxide systems include no stack gas reheat, relative conceptual simplicity, potential for NO_x removal, and the fact that the process has been demonstrated on a commercial scale and kinetic and design data are available. The major disadvantage of the process is the apparent higher operating costs due to high hydrogen requirements. Others include the mechanical complexity of the process and the difficulty of integrating a swing mode adsorption/regeneration section with a continuous SO_2 processing train. Due to its potential for simultaneous NO_x/SO_2 removal, the Shell/UOP process is recommended for further consideration.

References - DA-030, DA-147, NA-225, PO-109, SC-341, SL-062, SL-065, SL-080, UN-030.

DILUTE SYSTEM SULFATE REMOVAL FOR SODIUM DOUBLE ALKALI

Process/Subsystem Description - Flue gas is scrubbed with a clear, dilute solution of NaOH and Na_2SO_3. Spent scrubbing liquor is reacted with lime to regenerate the absorbent solution and precipitate calcium sulfate solids for disposal. The dilute mode of operation would generally be used for applications where the rate of oxidation is relatively high. The concentration of NaOH, Na_2SO_3, and $NaHSO_3$ is kept relatively low (below 0.15 M). The concentration of sulfate is greater than the concentration of sulfite, and calcium sulfate is precipitated in the regeneration step while NaOH is regenerated. In the Buell-Envirotech process, spent scrubbing liquor is oxidized to further increase the relative concentration of sulfate before the liquor is reacted with lime.

Environmental and Energy Considerations - SO_2 removal efficiencies of 95% or greater can be achieved. The process can remove particulates simultaneously with SO_2, but does not appear to be capable of NO_x removal. Disposal of the waste sludge could result in secondary pollution problems. Sludge from dilute systems, however, has a higher concentration of calcium sulfate than sludge from concentrated systems and should thus be disposed of more easily. Energy requirements for dilute systems would be greater than those for concentrated systems because a higher L/G is required due to the lower concentration of alkali in the scrubbing liquor. Stack gas reheat is required. The raw materials required are Na_2CO_3, which is used for sodium makeup and for softening of the regenerated liquor, and lime, which is used for regeneration.

Development Status - The dilute double alkali process has been tested by Envirotech at a 2500 acfm pilot plant, by Zurn Industries at a 20-30 Mw unit treating gas from coal-fired industrial boilers, and by General Motors at a 32 Mw unit treating gas from coal-fired industrial boilers. The process has been integrated. Commercial technology is used, and no scale-up problems are expected.

Economic and Technological Considerations - Chemical and mechanical complexity of the dilute double alkali process is comparable to that of the concentrated process. Equilibrium constraints limit the concentration of NaOH that can be produced in the regeneration step to 0.15 M. Because of the lower concentration of alkali in the scrubbing liquor, a higher L/G is required for the dilute process, and a higher volume of liquor must be handled by the solids separation equipment. Thus, capital costs for a dilute system may be higher than those for a concentrated system. Dilute systems, however, produce waste solids with a higher concentration of calcium sulfate. These wastes could be disposed of more easily than the calcium sulfite sludge from concentrated processes. The regenerated liquor in dilute systems has a high concentration of calcium so that gypsum scaling in the absorber can be a problem. Na_2CO_3 required as sodium makeup is used to soften the liquor by precipitating $CaCO_3$ to decrease the concentration of calcium ions and reduce the scaling potential.

Applicability - Applicability of the dilute process is comparable to that of the concentrated process. The process can be turned down, retrofitted, and modularized. Process sections can be decoupled by the provision of intermediate storage, but larger storage tanks would be required for a dilute process than a concentrated one since larger volumes of liquor are circulated.

Summary - Dilute double alkali systems appear to be superior to concentrated systems for applications where high rates of oxidation are encountered (for example, operation with low sulfur coal or high excess air). Because of the low concentration of alkali in the scrubbing liquor, sulfates are precipitated as $CaSO_4 \cdot 2H_2O$ with the addition of lime. NaOH is regenerated for recycle to the absorber. Dilute systems, however, require a higher L/G and are more prone to gypsum scaling. The dilute double alkali process will be considered as an alternative in the technical summary paper on the sodium double alkali process.

References - BL-110, CO-163, KA-143, KA-227, ZU-017.

DIRECT PRODUCTION OF SULFUR FROM $MgSO_3$

Process/Subsystem Description - This concept is an alternative in the magnesia slurry absorption process. In the magnesia slurry process the $MgSO_3$ is currently calcined to regenerate MgO and produce an SO_2 rich off-gas for sulfur or sulfuric acid production. This concept would produce elemental sulfur directly in the calciner while regenerating the MgO.

Producing sulfur in the calciner could probably be done either catalytically or non-catalytically with the catalytic approach offering potential advantages in shorter required residence times and lower temperature operation. There may however be problems with catalyst life. H_2/CO reducing gas could be produced from an oxygen or air blown gasifier. The gas leaving the calciner would contain sulfur mainly in the form of elemental sulfur, H_2S, and SO_2. The gas would be cooled to condense out the elemental sulfur. The gas would then be sent to catalytic converters to react the H_2S and SO_2 together to form sulfur by the Claus reaction. The gas stream would again be cooled to condense out sulfur and then be sent to the boiler or incinerated and routed back to the SO_2 absorber.

Environmental and Energy Considerations - There would be no secondary pollution associated with the process if the exiting gas stream from the last sulfur condenser was sent back to the boiler. The residual sulfur compounds would then be oxidized to SO_2 and recaptured in the SO_2 absorber. A suitable H_2/CO reducing gas is needed for the process to reduce the SO_2 to sulfur in the calciner. No other raw materials are needed for the process.

Development Status - A study has been performed to determine the thermodynamic feasibility of $MgSO_3$ decomposition with reducing gas and conceptual designs of possible process arrangements have been performed.

Since the feasibility study has shown that it is thermodynamically possible to produce sulfur in the calciner, the next step would be to perform bench- and pilot-scale testing of the concept. This would help determine if the kinetics of the reducing gas/SO_2 reactions were favorable and would identify potential equipment design problems with the process.

Economic and Technological Considerations - The process is mechanically very complex. If a catalyst is used in the calciner there will be a problem with MgO/catalyst separation. Also, the very small MgO particles will cause a large portion of the particles to be entrained in the exiting gas stream. This gas stream must be cleaned to very low particulate levels to prevent catalyst deactivation in the Claus-type catalytic converters.

Applicability - The process should follow load changes fairly well. Retrofitting this process modification into an existing MgO scrubbing system should be feasible. The existing calciner could possibly be used. The process could be difficult to modularize because of the cost advantages inherent in large-scale kilns. Process decoupling within the process would be difficult because reducing gas production must follow load. Decoupling of the regeneration section from the absorption section may be accomplished through intermediate slurry storage.

Summary and Conclusions - The concept of producing sulfur directly from $MgSO_3$ in the calciner of the MgO scrubbing process appears to be feasible. But the process is only conceptual and potential equipment problems still need to be identified and MgO/catalyst separation problems could exist if a catalytic reactor is used. The process will be discussed in the magnesia slurry technical summary paper as an alternate.

References - LO-R-154

DOUBLE ALKALI WITH LIMESTONE
(SHOWA-DENKO, KUREHA-KAWASAKI)

Process/Subsystem Description - SO_2 is absorbed in a solution of Na_2SO_3. The scrubbing solution is regenerated by reaction with $CaCO_3$ in series reactors near 212°F. Sulfates are removed by addition of H_2SO_4 to dissolve $CaSO_3$ and precipitate $CaSO_4 \cdot 2H_2O$. The process also includes forced oxidation of the sludge product to produce gypsum.

Environmental and Energy Considerations - Excellent SO_2 removal is possible. No other pollutants are removed. Secondary pollution problems could result from disposal of the gypsum product if it cannot be sold. Energy requirements are comparable to those for the sodium/lime double alkali process. Reheat will be required, but L/G and pressure drop are relatively low. Sodium carbonate make-up, limestone, and sulfuric acid are required as raw material.

Development Status - This process has been demonstrated commercially on oil-fired boilers in Japan, where it is offered by Showa-Denko and Kureha-Kawasaki. Some work has been done in the U.S. by A. D. Little.

Economic and Technological Considerations - This process is similar to the sodium/lime double alkali process in mechanical complexity, but is slightly more complex chemically. Na_2CO_3 makeup is minimal but 2-3 moles H_2SO_4 are required per mole of sulfate formed in the scrubber. Moderate to high levels of sulfate formation would thus be costly. Regeneration with limestone requires a long time at moderate temperature and requires an operation for Mg^{++} removal.

Applicability - This process is generally applicable for utility or industrial applications. It can be turned down easily, retrofitted, and modularized. Process sections can be decoupled. Applicability is somewhat limited by the need to market or dispose of large quantities of gypsum which although more easily dealt with than sludge, nevertheless requires land for disposal if the product cannot be sold.

Summary and Conclusions - This process scored very well compared to other throwaway processes. It is well developed, has good applicability, and scored well above average in Economic and Technological Considerations and above average in Environmental and Energy Considerations. The ability to use limestone rather than lime for regeneration is an advantage over the sodium/lime double alkali process, but the use of limestone requires a complex reactor system. Mg^{++} removal may be necessary to produce good quality, marketable gypsum. Somewhat higher levels of oxidation are acceptable for this process than for sodium/lime double alkali, but higher oxidation rates require increased H_2SO_4 consumption for sulfate removal. This process is recommended for further evaluation, but it will be discussed in the technical summary paper on sodium/lime double alkali rather than in a separate paper.

References - AN-056, AN-147, EN-445

DOWA ALUMINUM SULFATE PROCESS

Process/Subsystem Description - Basic aluminum sulfate ($Al_2(SO_4)_3 \cdot Al_2O_3$) absorbs SO_2 from a gas stream, forming $Al_2(SO_4)_3 \cdot Al_3(SO_3)_3$ which is sent to an oxidizing tower where the sulfite is oxidized to sulfate, forming $Al_2(SO_4)_3$. A small part of the oxidized solution is neutralized with limestone to reform $Al_2(SO_4)_3 \cdot Al_2O_3$ and produce gypsum. The gypsum is separated from the solution in a thickener and centrifuge and washed; the overflow, filtrate, and wash water are recycled to the absorber.

Environmental and Energy Considerations - SO_2 removal efficiencies of 99% have been achieved from acid plant tail gas. Removal is more difficult at higher temperatures, so that removal from boiler flue gas may be around 95%. The process does not appear to have potential for multipollutant removal. The system is basically operated as a closed circuit, but a small amount of overflow from a settler is discarded to keep the magnesium concentration low enough to produce marketable gypsum. Secondary pollution problems could result from disposal of the gypsum product if it cannot be sold. Energy requirements are similar to those for the sodium double alkali process, but the L/G will be higher. An L/G ratio of about 35-75 gallons/1000 scf will be necessary to achieve SO_2 removal from boiler flue gas. Stack gas reheat will be required. The major raw material required is limestone. A small amount of aluminum makeup will also be required to replace that lost in the gypsum.

Development Status - This process was developed by the Dowa Mining Co., Ltd., for eliminating SO_2 from the tail gas of double-contact sulfuric acid plants. Two units have been in operation at an acid plant since 1974. Another unit was put into operation on an oil-fired industrial boiler in 1976, and other units are under construction. There have been no applications to coal-fired boilers, however. All process steps have been integrated. Currently commercialized technology is used in the process and no scale-up problems are anticipated.

Economic and Technological Considerations - Overall, the process is similar in chemical and mechanical complexity to the sodium double alkali process. Limestone addition in the regeneration reaction must be controlled to carry the reaction to the optimum degree of completion. A magnesium removal loop must be added to limit magnesium concentrations in the gypsum product if the gypsum is to be marketed. The solubility relationships of aluminum salts can be complex.

Applicability - This process appears to be generally applicable for utility and industrial applications. It can be turned down, retrofitted, and modularized. Process sections can be decoupled. Applicability is somewhat limited by the need to sell or dispose of large quantities of gypsum which although less of a problem than sludge, requires land for disposal if the product cannot be sold.

Summary and Conclusions - This process scored very well in all four categories of the evaluation criteria. It appears to be a promising alternative to the sodium double alkali process in that it uses limestone rather than lime. The Dowa process can be operated at any level of oxidation and produces good quality gypsum rather than calcium sulfite sludge, but requires a higher L/G than the double alkali process and uses a countercurrent scrubber. A technical summary paper should be prepared on this process for further consideration.

References - AN-147, YA-075

DRY ALKALI PLUS FABRIC FILTER

Process/Subsystem Description - An alkali mineral such as nahcolite ($NaHCO_3$) or trona ($NaHCO_3$ and Na_2CO_3) is brought into direct contact with flue gas to react with the SO_2. The flue gas exits the plant through a fabric filter in a baghouse. The spent alkali mineral collected by the filter is then discarded. Alternatively, dry alkali minerals could be brought into contact with flue gas by direct injection or in a countercurrent moving bed.

Environmental and Energy Considerations - SO_2 removal with fabric filters is somewhat limited. SO_2 removals of up to 90% have been achieved with moving beds. Fine particulates are also removed, and NO_x may be removed in the countercurrent moving bed. The disposal of the spent alkali mineral poses a serious problem, with potential for severe secondary pollution. Energy requirements for these systems should be low since no reheat is required and pressure drop should be acceptable.

Development Status - The use of dry alkali minerals with fabric filters for SO_2 removal has been demonstrated on a commercial oil fired power generation boiler and tested on commercial low sulfur coal fired power generation boiler (~11 MW). The process has been partially integrated. Current technology is used, and no scale-up problems are anticipated.

Economic and Technological Considerations - Fabric filter SO_2 removal systems are slightly more complex, chemically and mechanically, than double alkali systems. SO_2 removal is somewhat limited, but dry product is collected and no corrosion problems are experienced as they would be in a scrubber.

Applicability - Applicability of fabric filters is limited. They can be modularized easily and can be turned down, but retrofits may be difficult due to space limitations. Applicability is further limited to areas where a source of low cost sodium alkali is available and where the Na_2SO_3/Na_2SO_4 waste product can be disposed of in an environmentally acceptable manner.

Summary and Conclusions - This process scored above average compared to other throwaway processes. Applicability is poor, but the process scored above average in the other categories. They key disadvantages are the limited availability of low cost sodium alkali and the difficulty of waste disposal. The process is limited to application with low to moderate sulfur coal because of the expense of makeup sodium alkali. However, the process achieves good fine particulate removal, produces a dry product, does not require reheat, and avoids the corrosion problems associated with scrubbers. This process is recommended for further consideration and will be included in a general discussion of sodium throwaway systems.

Reference - BE-465

DRY REMOVAL WITH GROUND LIME

This process, developed by Dr. Thomas W. Weber and Dr. Wienert of SUNY at Buffalo, involves diverting the combustion gases into a reactor where they are mixed with fine particles of lime-containing materials for up to 15 seconds. The majority of the solid particles are settled out in a settling chamber, and the gases returned to their normal flow. Part of the settled material is ground together with fresh lime particles and charged into the reactor.

Some experimental studies were made, but the process is apparently still at the conceptual stage. The experimental studies formed the basis for a patent application. Due to its conceptual status, insufficient information is available to evaluate the process completely at this time and the process is not recommended for further consideration.

References - WE-337, WI-281

DRY SORBENT PROCESS

Dr. J. O. L. Wandt, Dave Pershing and others from the Department of Chemical Engineering at the University of Arizona found in the course of other investigations that certain dry sorbents would remove SO_2 if NO_x were also present in the gas. An unsolicited proposal was submitted to EPA, but the request for funds was turned down and development ceased. The process did not advance beyond the conceptual state and is not recommended for further consideration.

Reference - PE-270

EBARA-JAERI PROCESS

Process/Subsystem Description - The Ebara-Jaeri Process employs an electron beam to simultaneously remove SO_2 and NO_x from flue gas. High efficiency electrostatic precipitators remove particulates before the gas is irradiated. A powder consisting of compounds of S, N, O, and H and a sulfuric acid mist is then generated in the electron beam reactor. Removal of the by-products is accomplished in another electrostatic precipitator before the gas is exhausted through the stack.

Environmental and Energy Considerations - At 400 ppm concentrations of NO_x and SO_2, removal efficiencies at 2 atm. are shown as 80% and 75%, respectively. Removal efficiencies decrease with increased concentrations, and it appears the SO_2 removal in a coal-fired boiler application would be quite poor (∿60%). Disposal of the by-products may present a secondary pollutant problem. Although no reheat and no reducing gas are required, electrical energy requirements are high for this process.

Development Status - This process is in the early stages of development, and little is known about it. Bench-scale testing has been done, using oil-fired flue gas, but it has not been tested on coal-fired gas. The process is not fully integrated, and the method of disposal of by-products has not been specified. The technology utilized is rather novel and may not be available commercially. There are many potential scale-up problems.

Economic and Technological Considerations - Process control may be difficult, due to control problems with the accelerator. Very little information is available from which a judgment can be made. The bench-scale unit was made of stainless steel, but the by-product material formed is corrosive toward stainless steel.

Applicability - Very little information is available from which a judgment can be made about the applicability of this process. SO_2 removal appears to be inadequate and utility acceptance could be a problem.

Summary and Conclusions - Although this process has not been fully developed, it suffers from low SO_2 removal. It is not recommended for further consideration.

References - FA-149

FORCED OXIDATION OF $CaSO_3$

Process/Subsystem Description - Forced oxidation systems increase the amount of sulfite which is oxidized to sulfate. In lime or limestone systems this is generally done by sparging air into the hold tank. Forced oxidation can be applied to the waste solids from lime/limestone or double alkali processes, or can be carried out within the scrubber loop.

Environmental and Energy Considerations - Forced oxidation of waste solids should not affect SO_2 or multipollutant removal ability of lime/limestone or double alkali systems. Oxidation within the scrubber loop of lime/limestone systems, however, may decrease SO_2 removal capability because the concentration of sulfite is decreased. Sufficient limestone solids must then be present in the scrubber to provide alkalinity for effective SO_2 removal. Alternatively, mass transfer additives could be used to provide the alkalinity necessary for good SO_2 removal. Forced oxidation does not affect capability for multipollutant control. Secondary pollution problems should be diminshed in systems using forced oxidation. The resulting calcium sulfate (gypsum) crystals are larger, more easily dewatered, and stronger than calcium sulfite. As a result, the gypsum is suitable for disposal by landfill. In Japan, systems using forced oxidation produce marketable gypsum.

A liquor purge stream may be necessary to control soluble species in solution, but this purge would be no larger than that which would be discharged with the waste solids from systems not using forced oxidation. Sulfuric acid addition is generally required to decrease pH and dissolve calcium sulfite to increase the rate of oxidation. Limestone utilization may be improved since the air sparge will tend to sweep CO_2 from the liquor, allowing more limestone dissolution in the hold tank.

The use of forced oxidation will require additional energy to operate the air compressors, but the amount should not be excessive.

Development Status - Systems for forced oxidation of waste solids are commercial in Japan on limestone and double alkali systems. In the U.S., Pullman Kellogg Company is offering commercially a slurry process with magnesium additive and oxidation of waste solids. Forced oxidation in the scrubber loop has also been tested with lime/limestone systems, and is used in the Dowa and Kurabo double alkali processes. Forced oxidation uses commercial technology, and should not present scale-up problems.

Economic and Technological Considerations - In general, forced oxidation should increase overall process complexity. However, the equipment required for it is relatively simple, and it will make solids handling and disposal easier. Thus, its use may improve the process.

Applicability - The use of forced oxidation should improve applicability of lime/limestone or double alkali processes. Oxidation of waste solids should not affect retrofitability, turndown capability, decoupling ability, or industrial modularization, but will make waste disposal easier by imrpoving the quality of the solid waste. Oxidation within the scrubber loop, however, may complicate retrofits and affect turndown capability.

Summary - The use of forced oxidation appears to be a promising alternative for improving the quality of solid wastes from lime/limestone or double alkali processes. Energy consumption will be increased somewhat, but a more desirable waste product with a higher solids content will be produced.

References - AN-147, RO-333

GRILLO PROCESS

Process/Subsystem Description - The Grillo Process uses an aqueous solution of manganese oxide and magnesium oxide to absorb SO_2. Absorbtion is carried out with cocurrent circulation of an aqueous MgO/MnO solution and the flue gas. A side stream of slurry is withdrawn and the rest recirculated to the scrubber. The side stream is dried, mixed with coal, and calcined in a fluid bed calciner to convert the magnesium sulfite/sulfate and manganese sulfite/sulfate to their oxide forms. Sulfur dioxide off gas is sent to a sulfuric acid plant. The regenerated absorbent is recycled to the scrubber and a side stream is treated for ash removal before it is also recycled to the absorber.

Environmental and Energy Considerations - To date the Grillo process has been used on oil-burning power plants and sulfuric acid tail gases. Reported SO_2 removal efficiencies of 90 to 95 percent have been achieved. Other than some fly ash removal in the scrubber, the Grillo process has not been reported effective in removing any other pollutant. The limitations on the process' ability to increase SO_2 removal efficiency from 90 to 95 percent or higher is unknown. Secondary pollutants from the Grillo process include an ash stream and toxic manganese compounds which may be produced during its operation. After passing through the scrubber, the stack gas requires some reheat. However, because the absorption of the SO_2 occurs relatively fast, the stack gases are not cooled to saturation in the scrubber. No reducing gases are required for the scrubber solution regeneration. The L/G ratio for the scrubber is about 6 or 7 and the pressure drop through it is less than 1 psi. Raw material requirements for the Grillo process include $MgSO_4$, H_2SO_4, MnO_2, and coal.

Development Status - The process has been tested in a 12,000 scfm pilot plant on a sulfuric acid plant tail gas and in a 16,000 scfm unit at a power plant in Germany. Grillo considers the process developed and has offered it commercially. The process uses commercialized technology. Some scale-up problems may be encountered because of solids handling problems. Development on the process has slowed to a virtual standstill. No full scale units are currently planned.

Economic and Technological Considerations - The chemistry of the Grillo process is complex but evidently workable. Likewise, the mechanical complexity of the process would be categorized as relatively complex due to the number of processing steps required. The process is slightly more complex than the Magnesium Oxide process.

Applicability - If the Grillo process were used in coal-fired power plant service, a pretreatment step for fly ash removal would be necessary. Besides the fly ash no other species need to be removed from the flue gas. Because of low pH's and high temperatures minor use of some special materials will be necessary. The process produces an SO_2/air stream which may be sent to a sulfuric acid plant. No other by-products are formed. Retrofitting a power plant with the Grillo FGD process would probably require minor modifications due to the process' mechanical complexity. The process possesses turndown capability, decoupling ability, and modularization potential.

Summary and Conclusions - The Grillo process rated high in the preliminary evaluation of the wet regenerable FGD processes. It is comparable in many respects to the Magnesium Oxide process. The Grillo process' advantages include those which are inherent to regenerable processes: minor disposal problems and reduced raw materials makeup costs. Other advantages include good by-product marketability and minor plugging and scaling problems in the scrubber. Compared to the Magnesium Oxide process, the Grillo process offers advantages of higher SO_2 absorption rates and easier regeneration due to manganese oxide addition. Disadvantages of the Grillo process include high energy requirements for regeneration, solids handling problems, and corrosion problems. Relative to the Mag-Ox process, the Grillo process has the following disadvantages: increased chemical complexity due to the MnO addition and potential for toxic manganese compounds being formed and released to the environment. This process is recommended for further evaluation. It will be discussed in the Magnesium Oxide technical summary paper.

References - SL-070, CA-327

HÖLTER

Process/Subsystem Description - This process has been developed in West Germany by Saarberg-Hölter. SO_2 is absorbed in a 0.5-10 wt. % clear solution of $CaCl_2$ saturated with lime. A special additive called "Absorben 75" is also added. This additive is said to control the pH of the solution, thus helping to prevent corrosion, and to increase SO_2 removal by increasing the concentration of calcium ions and preventing scaling in the scrubber. Spent scrubber solution is oxidized to produce gypsum, and slaked lime is added to replace the calcium ions lost in the gypsum.

Environmental and Energy Considerations - SO_2 removal efficiencies of 90-95% have been achieved with this process. HCl and HF may also be removed. Secondary pollution may result from disposal of the gypsum product. Energy requirements are relatively low. Because of the concentrated scrubbing solution, scrubber temperature is higher than in most wet scrubbers so that less reheat may be required. Energy requirements for the combination of L/G and pressure drop are also relatively low. Lime and "Absorben 75" (formic acid) are required as raw materials. HCl makeup may be required if the chloride level in the coal is very low.

Development Status - The Hölter process has been demonstrated at a 40 MW coal-fired power plant and at a 10 MW equivalent plant for purification of gas from a waste product incinerator. The process has been fully integrated. Current technology is used in some, but not all, processing areas. No scale-up problems are anticipated.

Economic and Technological Considerations - The process is fairly simple chemically. Scaling is apparently averted due to short contactor residence times and the use of the mass transfer enhancement additive. Use of a scrubber solution high in chloride may require special materials of construction.

Applicability - This process can be turned down, retrofitted, modularized, and decoupled. Although gypsum is a more desirable product than sludge, requiring up to 60% less space for disposal, applicability may still be limited by land requirements if the product must be landfilled.

Summary and Conclusions - This process scored well above average compared to other throwaway processes. It did not score as well in Applicability or Economic and Technological Considerations as the top rated throwaway processes, but it is well-developed and scored above average in Environmental and Energy Considerations. The process developers claim over 20,000 hours of operation without scaling. Lime (rather than limestone) is required. This process is recommended for further consideration.

HORMEL PROCESS

Process/Subsystem Description - The process involves the reduction of SO_2 and SO_3 by CO over a lanthanum titanate catalyst. Elemental sulfur is produced and is collected in an electrostatic precipitator. Oxygen in the flue gas must be reduced to below one percent by passing the flue gas through a bed of glowing coke. This not only eliminates the contained oxygen but also generates CO for the subsequent reduction reaction. The use of an auxiliary boiler operated under reducing conditions to supply CO has also been proposed.

Environmental and Energy Considerations - Removal of SO_2 in excess of 95% is claimed for the process. Some reduction of flue gas NO_x may occur. Introducing large amounts of CO to the flue gas followed only by a catalyst bed and ESP would probably result in large CO emissions. Coke usage rates have not been defined, but probably represent a major operation cost.

Development Status - The Hormel process has not been developed past the laboratory investigation stage and no development work is in progress at this time.

Economic and Technological Considerations - The process does have the inherent advantage of being dry, and of producing elemental sulfur directly. However, the low space velocities proposed for the coke bed would probably result in a prohibitively large vessel. Also the maintenance of a glowing coke bed and the use of a fixed bed catalyst reactor on flue gases may be impractical. The process can be regarded as fairly complex both from a chemical and mechanical standpoint.

Applicability - Retrofit of the process would be difficult because it requires rerouting of the plant flue gas system. The process should be relatively easy to turn down but simultaneous control of the carbon monoxide generation system could present serious problems. Sulfur is produced as a byproduct.

Summary and Conclusions - The process seems to have serious technical problems, mainly in the area of carbon monoxide emissions. These, combined with its very early development status and lack of current development interest, lead to the recommendation that further evaluation not be undertaken.

Reference - CH-407

HOUDRY

Process/Subsystem Description - The Houdry process involves catalytic absorption of SO_2 on a fixed, pelletized sorbent bed. The sorbent, a mixture of copper and silica oxides with a proprietary additive said to enhance the rate of adsorption, is regenerated with hydrogen gas to produce a concentrated H_2S stream suitable for conversion to elemental sulfur. Both adsorption and regeneration occur at approximately 600°F. Excellent sorbent activity and stability is reported through many cycles of operation.

Environmental and Energy Considerations - No data on SO_2 removal efficiencies or process energy consumption are available. Based upon data from other copper oxide processes, SO_2 removal greater than 90% and some NO_x removal could be expected. It appears that the process presents no secondary waste disposal problems. The process requires a H_2 reducing gas and should have an intermediate pressure drop.

Development Status - The process has not been developed beyond the laboratory scale. Houdry discontinued work on the process in 1970 and there seems to be no effort underway at this time.

Economic and Technological Considerations - The process is mechanically complex using large, relatively high temperature reactors. The necessity of having a hydrogen reducing gas greatly increases both its chemical and mechanical complexity and adds to its overall unattractiveness. The process would have limited turn down ability and integration of the batch absorption and regeneration with a continuous H_2S treating system would present difficulties.

Summary and Conclusions - This process was rated low compared to other dry processes because of its low development status and limited applicability. Development of the process has ceased. This is due to the disadvantages of the process including mechanical problems and high hydrogen requirements. This process should not be considered further.

References - HA-653

ICI STEAM STRIPPING PROCESS

Process/Subsystem Description - In this process, SO_2 is absorbed in a solution of $Al_2(SO_4)_3$ which buffers at pH 3-4. The solution is stripped by steam at 176-212°F to produce concentrated SO_2 gas which may be converted to H_2SO_4 or sulfur. Steam consumption is minimized by cooling the flue gas to 95-120°F before absorption. Sulfate is removed by neutralization of scrubbing solution with $CaCO_3$ to give gypsum.

Environmental and Energy Considerations - The SO_2 removal efficiency is reportedly good. The process has no potential for multipollutant removal, however. A small amount of gypsum is produced and must be disposed of. Stack gas reheat is required, but no reducing gas is needed. Steam requirements for regeneration are low compared to the Wellman-Lord process. The pressure drop in the scrubber is not large. Raw materials inlcude aluminum sulfate and limestone.

Development Status - This process was developed and used commercially in England to treat smelter gases in the 1930's. The process has not been integrated for utility application. Except for the gas cooling step, the process uses current technology. Scale-up problems would be associated with the gas cooling equipment.

Economic and Technological Considerations - The chemistry of the process is simple and straightforward. However, mechanically, the nonadiabatic gas cooling will require either exotic materials for heat exchange or complex design and operation.

Applicability - The process should be applicable to utility operation. It has potential for turndown, retrofitting, and being modularized. However, decoupling would be a problem due to low SO_2 loading of the absorbent.

Summary and Conclusions - The ICI steam stripping process ranked fairly high among the wet regenerable processes evaluated. Primary reasons for the high rating include relatively simple process chemistry and an advanced state of development. Advantages of the process include lower steam requirements relative to the Wellman-Lord process and easier handling of the sulfate/chloride solid wastes. Disadvantages include the high costs and questionable feasibility of nonadiabatic flue gas cooling. This process concept should be examined further as part of the sorption/steam stripping evaluation.

References - AP-029

IN SITU REDUCTION WITH CO

Process/Subsystem Description - SO_2 in flue gas is reduced to sulfur with carbon monoxide. The reduction is carried out over a copper-on-alumina catalyst at a temperature of 1000°F or greater. The combustion unit would be operated with little or no excess air so that the gas would contain at least the stoichiometric amount of CO required to react with the SO_2. The CO can also react with the sulfur formed to produce COS. Workers at the University of Massachusetts propose avoiding the problem of COS emission by operating at a temperature greater than 1500°F so that COS is not formed.

Environmental and Energy Considerations - SO_2 removal of 90% or more can be achieved. The developer claims that NO is also removed. Severe secondary pollution can result from formation of COS and CO. Formation of COS can be minimized by keeping the level of CO at stoichiometric or below, but SO_2 removal would then be reduced. Pressure drop should be relatively low. No stack gas reheat is required, but in retrofit applications, the gas may have to be heated up to absorption temperature. Additional CO reducing gas may be required. Makeup catalyst is the only raw material required.

Development Status - The process has been tested by Chevron Research Company in small scale tests, but was not fully integrated. Use of noncommercial technology would probably be required for the catalytic reactor. Serious scale-up problems would probably be experienced.

Economic and Technological Considerations - The process is relatively complex, chemically and mechanically. Operation of the boiler at low excess air to produce the required amount of CO would be difficult. Excess CO formation would result in production of COS. Insufficient CO would reduce SO_2 removal. Operation of the boiler under reducing conditions would result in problems such as increased boiler slagging, danger from flameouts, and potential for accelerated corrosion and deposits. Catalyst poisoning could also be a problem.

Applicability - The process produces sulfur as a by-product and should be suitable for industrial modularization. However, the process would be difficult to retrofit because of the high temperature required. Turndown would also be difficult. The process cannot be decoupled. Utility acceptability may be a problem in view of difficulties in retrofit, operating complexity, and potential secondary pollution problems.

Summary and Conclusions - This process scored low compared to other dry processes. Emission of COS and CO could be a severe secondary pollution problem. Operation of the boiler at low excess air as required by the process would be quite difficult. The process is relatively undeveloped and may present serious scale-up problems. Applicability of the process is also low. This process is not recommended for further evaluation.

References - CA-327, SL-070.

IN SITU REDUCTION WITH H_2S

Process/Subsystem Description - SO_2 in flue gas is catalytically reduced to sulfur with H_2S at a temperature of about 210°F. Sulfur formed is condensed in the catalyst. After accumulating a loading, the catalyst is removed and heated to remove the sulfur. In the Peter Spence process, a hot mixture of CO, H_2O, and H_2 is used to convert product sulfur to H_2S for recycling to the converter. In a similar process developed by Princeton Chemical Research, Inc., product sulfur is reacted with methane and steam to produce H_2S. The H_2S is injected into the gas, and the mixture is passed over a catalyst at 200-300°F. In the Ontario Research Foundation process, catalyst is treated with hot reducing gases at 570-930°F to condense the sulfur.

Environmental and Energy Considerations - SO_2 removal of 90% or greater should be possible. The process does not appear to be capable of multipollutant removal. Secondary pollution could result from emission of H_2S. No stack gas reheat is required, and pressure drop should be relatively low. Reducing gas is required, however, and additional energy is needed to heat up the catalyst bed to remove the condensed sulfur. Therefore, energy requirements could be relatively high compared to other FGD processes.

Development Status - The process has been tested in small scale tests and at the pilot plant level, but was not fully integrated. Development has apparently ceased. The process does not use commercial technology in most process sections. Serious scale-up problems may be encountered.

Economic and Technological Considerations - The process is relatively complex, chemically and mechanically. Catalyst poisoning was a serious problem in the pilot plant tests. Oxidation of H_2S by the oxygen in the flue gas can also be a problem. Valves and duct work required for switching between catalyst beds would be complex.

Applicability - The process should be suitable for industrial modularization. However, the process may be difficult to turn down and retrofit, and it cannot be decoupled. Sulfur is produced as a by-product. Acceptability to the utility industry may be a problem due to potential for H_2S emissions.

Summary and Conclusions - This process scored relatively low compared to other dry processes. Catalyst poisoning was a serious problem in the pilot plant tests. Generation of H_2S would also be difficult and expensive. The process is relatively undeveloped, and development work has apparently ceased. This process is not recommended for further evaluation.

References - CA-327, SL-070.

INSTITUT FRANCAIS DE PETROLE (IFP)

Process/Subsystem Description - In the IFP wet Claus Process an H_2S-SO_2 stream is reacted at relatively low temperature in an organic solvent to produce molten elemental sulfur. The process is applicable to ammonia scrubbing systems which produce a solution that can be evaporated to give a mixture of SO_2, NH_3, and H_2O. H_2S can be formed in situ to produce the required 2:1 H_2S-SO_2 ratio. Ammonia does not react and can be recycled to the absorber. Product sulfur is removed from the bottom of the reactor to go to sales or storage.

Environmental and Energy Considerations - While the wet Claus Process itself is not a large energy consumer, the production of H_2S in the IFP reactor is a relatively large consumer of reducing gas.

Development Status - IFP's "Liquid Claus" reactor is considered fully developed technology, as more than 20 of the units exist in commercial installations.

Economic and Technological Considerations - Integration into a system processing H_2S produced from coal based reducing gas has not been fully demonstrated. Otherwise the "Liquid Claus" technology has been fully demonstrated and presents no unresolved technological problems. While the sulfur production process is a minor contributor to the operating costs of an integrated ammonia system, the Claus gas preparation area, with relatively high fuel and reducing gas requirements, contributes significantly to the operating costs of the integrated system.

Applicability - The IFP regeneration section can easily be decoupled from the absorber section, and thus could be located anywhere on a plot.

Summary and Conclusions - This subsystem is in commercial use but has not been fully demonstrated on H_2S produced from a coal based reducing gas. Although the operation of this subsystem is a minor contributor to operating costs, gas preparation, due to the high fuel and reducing gas requirements, contributes significantly to the operating costs of an integrated FGD system. This subsystem was not recommended for further evaluation in lieu of a more direct subsystem for converting SO_2 to sulfur.

References - OT-R-051, SL-070

INTEGRATED CAT-OX PROCESS

Process/Subsystem Description - In the integrated Cat-Ox process, hot flue gas (700°F) is treated in high efficiency, hot electrostatic precipitators for particulate removal and then SO_2 is oxidized to SO_3 over a vanadium pentoxide catalyst. The hot gas is then run through the economizer and air preheater before being countercurrently contacted with a 78% sulfuric acid solution for removal of SO_3. The 78% sulfuric acid is then removed from the process as a by-product. Clean flue gas is sent to the stack. A modification of the integrated process for retrofit is called the Reheat Cat-Ox process. In such a system, the cooled flue gas must be heated before catalytic conversion can take place.

Environmental and Energy Considerations - Maximum SO_2 removal efficiencies for the Integrated Cat-Ox process have been reported at 93 to 95 percent. The process is also effective for removing the original quantity of SO_3 in the flue gas, halogen compounds, and particulates in the pretreatment step. NO_x removal has not been experienced. The ability of the Cat-Ox process to achieve greater than 93 to 95 percent SO_2 removal is limited by the reaction kinetics in the catalytic oxidation step and by equilibrium conditions in the absorber which affect acid removal efficiency. Secondary waste streams from the Cat-Ox process include fly ash and vanadium pentoxide catalyst solids, sulfuric acid, leakage from the acid pump seals, and sulfuric acid mist which passes through the absorber demister pads. There are no reheat requirements for the stack gas after it exits the absorber because of the high absorber operating temperature. No reducing gas is required for the Cat-Ox process. Overall pressure drop for the Integrated Cat-Ox process is about 26 inches H_2O. The L/G ratio for the acid absorber is unknown. The only raw material required for the process is the vanadium pentoxide catalyst. There are currently no availability problems with this catalyst.

Development Status - The process was first tested as a 15 MW integrated prototype operating on part of the stack gas from a 250 MW boiler. In 1970, the EPA and Illinois Power funded a full-scale demonstration of a Reheat Cat-Ox system on an existing 110 MW coal-fired unit. The system was ready for operation by mid-1973. The Cat-Ox process uses commercialized technology in all of its process sections. For this reason, and the demonstration of a 110 MW unit, no scale-up problems are anticipated.

However, an Integrated Cat-Ox system for new boiler application on a large scale has not been built to date.

Economic and Technological Considerations - The chemistry of the process is simple and has been demonstrated on a large scale. The mechanical design of the system would be classified as slightly complex because of the processing steps involved in acid production.

Applicability - Particulates, chlorine, and fluorine compounds in the stack gas will interfere with the operation of the Cat-Ox process if present in large quantitites. The particulates can be effectively removed to a safe level by electrostatic precipitators. Fluorine is a possible catalyst poison as is chlorine. Flue gas concentrations of chlorine and fluorine will probably not be in large enough concentrations, though, to cause appreciable catalyst poisoning. Minor use of special materials is required for the Cat-Ox acid absorber because of the problem of producing hot, dilute acid during start-up of the system. The marketability of the by-product acid is restricted to fertilizer production due to the acid concentration (78% H_2SO_4) and impurities in the acid. The Integrated Cat-Ox system is very difficult to retrofit to existing boilers because of the requirement that the air heater and economizer be relocated or significant duct work be done. The Reheat Cat-Ox system loses much of its competitiveness because of the energy that must be added to the air to heat it to reaction temperature. The process cannot be decoupled.

Summary and Conclusions - Integrated Cat-Ox system would seem to have some significant advantages when applied to new boiler service. It appears to have low energy requirements, and produces no undesirable by-products. Its disadvantages are the requirement for very high efficiency hot electrostatic precipitators, a less marketable product compared to elemental sulfur, and difficulty of demonstrating an integrated system. This process should be considered for further evaluation because of its high potential and relatively simple chemistry.

References - BE-326, BR-272, CA-268, EV-022, JO-049, MA-481, MO-179, PH-029, SL-070, SO-005, WA-215

IONICS ELECTROLYTIC REGENERATION PROCESS

Process/Subsystem Description - Ionics has developed a subsystem that consists of an electrolytic cell which electrolyzes moderately concentrated sodium sulfate solutions to sulfuric acid and sodium hydroxide, both of which also contain some sodium sulfate. The basic cell can be modified by the addition of another membrane to produce a pure dilute sulfuric acid solution in order to purge sulfate formed by oxidation. This subsystem can be used as a regeneration step for an alkaline scrubbing system or as a means of converting a sodium sulfate purge from other processes back into usable form.

Environmental and Energy Considerations - Assuming this subsystem is used as a regeneration step for an alkaline scrubbing system, SO_2 removal efficiencies of greater than 90 percent are quite possible from the integrated system. NO_x removal efficiencies of 20 to 40 percent may also result. The dilute sulfuric acid produced may cause a disposal problem in some applications. The Ionics process is a large consumer of electric power.

Development Status - The Ionics process has been piloted at the 0.75 MW level on coal-fired flue gas. Almost all of the development work has been finished on the cells, although minor modifications are still continuing to reduce the cell voltage.

Economic and Technological Considerations - The economics of the process may be improved by the use of cheaper off-peak power for regeneration. However, capital costs would consequently be increased because of necessary increased regeneration cell and storage capacity.

Applicability - The process should not be limited for new plant applications. The large plot area requirements may limit retrofit applications.

Summary and Conclusions - This subsystem was developed to make sodium alkali scrubbing systems producing sodium sulfite regenerable. However, because of the high energy and capital cost associated with the electrolysis of the sodium sulfite, it is unlikely that the subsystem can compete against other regenerable processes. Consequently, this subsystem was not recommended for further evaluation.

References - OT-R-51

IPRAN PROCESS

Process/Subsystem Description - The gas is scrubbed with ammonia in a specially designed venturi scrubber. The effluent scrubbing solution is mixed with phosphoric acid in a heated vessel and stripped of SO_2 in a second venturi-type vessel with a stream of air. The concentrated SO_2 can be used for acid or sulfur production. The ammonium phosphate solution (mostly $NH_4H_2PO_4$) is sent to an associated complex fertilizer plant.

Environmental and Energy Considerations - Good SO_2 removal (>90%) should be possible with this process. No other pollutants will be removed. Secondary pollution can arise from ammonia plume formation or from disposal of the ammonium phosphate if it cannot be sold. No reducing gas is required, and L/G and pressure drop should be low. An additional venturi will be required for air stripping, however. Gas reheat will be required, and steam is required to heat the mixing vessel. Ammonia and phosphoric acid are the raw materials required.

Development Status - Applications of this process are reported to be operating successfully in at least three sulfuric acid plants in Romania, where the process is considered to be commercially developed. It has not been tested in a utility application.

Economic and Technological Considerations - This process is more complex, both chemically and mechanically, than the sodium double alkali process. Scrubber design is complicated by the volatility of the ammonia and the possibility of plume formation. Large amounts of acid are required for acidulation because of the low reactivity of phosphoric acid.

Applicability - Operating characteristics of this process should not seriously limit its applicability for utility or industrial application. The process can be turned down, retrofitted, and modularized. Process sections can be decoupled. Applicability is, however, limited to areas where a market for the ammonium phosphate fertilizer exists. A concentrated stream of SO_2 is also produced as a by-product.

Summary and Conclusions - This process did not score well compared to other throwaway processes due to its complexity and secondary pollution problems resulting from ammonia plume formation. Applicability is limited to areas where the ammonium phosphate is marketable for fertilizer production. This process is not recommended for further consideration.

References - CA-327, SL-070, TE-188

ISHIKAWAJIMA-HARIMA HEAVY INDUSTRIES PROCESS

Process/Subsystem Description - This process removes NO_x and SO_2 from flue gas by oxidizing nitric oxide with ozone and absorbing the resulting nitrogen dioxide along with sulfur dioxide. The sorbent is a lime or limestone slurry containing copper and sodium chloride. The flue gas passes through a prescrubber before it is oxidized, passed through the absorber, reheated, and exhausted from the stack.

Environmental and Energy Considerations - Pilot plant testing on an oil-fired flue gas has shown 90% SO_2 removal and 80% NO_x removal. An environmental problem may be present in the disposal of by-product gypsum, and a wastewater treatment system will be required to prevent the discharge of excess nitrogen compounds. Particulates and chlorides are removed in the prescrubber. Reheat is required; reducing gas is not. Ozone is required, and production of ozone is a very energy intensive process. The L/G necessary for 80-90% NO_x removal is 60-75 gal/Macf. Raw materials required are calcium carbonate, sulfuric acid, slaked lime, copper chloride, and sodium chloride.

Development Status - The process has not been demonstrated on flue gas generated from coal. It has, however, undergone testing as an integrated process at the pilot plant level, using flue gas from an oil-fired boiler. The process configuration for removal of complex sulfur nitrogen compounds and nitrate salts has not been finalized. A decision has not been made as to the method of treatment of the wastewater. Currently, commercialized technology is utilized in most of the process. Scale-up problems are probable because of the lack of testing on coal and the wastewater treatment requirement.

Economic and Technological Considerations - This process is not as complex as some of the other SO_x/NO_x processes, but it is more complex than the flue gas desulfurization processes. Most of the equipment will be polymer-lined carbon steel, but some pieces of equipment will have to be Inconel 625, stainless steel, or glass-lined steel.

Applicability - This process has been judged easy to retrofit if sufficient land is available. Load following capabilities are also potentially good. By-product gypsum will probably have to be land-filled, as it probably cannot compete with other sources of gypsum.

Summary and Conclusions - This process was rated below average. Although it removes SO_2 and NO_x simultaneously, it requires an ozone generator and flue gas reheat. It also has not been tested on coal-fired flue gas and wastewater treatment methods have not been specified. The Ishikawajima-Harima Heavy Industries Process is not recommended for further consideration.

References - FA-149

JOHNSTONE ZINC OXIDE

Process/Subsystem Description - This process is based on the absorption of SO_2 by Na_2SO_3 which is regenerated by ZnO to give $ZnSO_3$ solids. The $ZnSO_3$ solids are dried and then calcined at 600-700°F to give ZnO and concentrated SO_2. Sulfate formed in the scrubber is removed from solution in a two step process. First, SO_2 gas and $CaSO_3$ solids are reacted with the scrubber outlet solution. Calcium sulfate solids are crystallized and separated out. The return solution is reacted with lime to crystallize the separate calcium sulfite solids.

Environmental and Energy Considerations - The SO_2 removal efficiency for this process is around 90%. It has no multipollutant removal capability, but it can potentially improve its SO_2 removal performance. Secondary pollutant problems are limited to a small amount of $CaSO_4$ which must be disposed of as well as potential zinc compound emissions. The flue gas requires reheat but pressure drop through the scrubber is not large. Reducing gas is not needed for regeneration, however, fuel is required for drying and calcining $ZnSO_3$. Raw materials include ZnO, Na_2SO_3, and lime.

Development Status - The Johnstone process was tested in a 1000 cfm, coal-fired pilot plant in 1937. It was only partially integrated. The process uses current technology and minor scale-up problems are anticipated.

Economic and Technological Considerations - The chemistry of the process is basically fairly simple. Mechanically the system requires a number of operations but each is well understood. The scrubber design is simple, but prescrubbing of the gas would probably be desirable for chlorides removal. The regeneration operation is mechanically complex.

Applicability - The ZnO raw material supply might be a problem. Oxidation problems would possibly eliminate the process' applicability to low-sulfur coal since the sulfate product is nonregenerable and must be removed by crystallization. The process can be turned down, retrofitted, and modularized. Decoupling should be possible.

Summary and Conclusions - The Johnstone Zinc Oxide process rated high among the wet regenerable FGD processes evaluated. Its advantages include good SO_2 removal, chemical simplicity, and low energy requirements. Primary disadvantages include the potential raw material supply problem for ZnO, and the possibility of discharge of toxic zinc compounds. For these reasons, the process is not recommended for further consideration.

References - MC-307

KAWASAKI MgO/LIME PROCESS

Process/Subsystem Description - Flue gas is scrubbed in a multiventuri type scrubber with a slurry containing calcium and magnesium sulfites. The SO_2 reacts to form bisulfites. A portion of the sulfite-bisulfite slurry is oxidized by bubbling air to produce gypsum and magnesium sulfate. Sulfuric acid may be added to the slurry prior to oxidation to adjust the pH. The gypsum-slurry from the oxidizer is treated in a thickener and centrifuged. Most of the thickener overflow is recycled to the absorber; a portion is sent to a reactor and reacted with lime and magnesium to precipitate gypsum and magnesium hydroxide. The resulting slurry is sent to the absorber.

Environmental and Energy Considerations - SO_2 removal efficiencies of about 90% have been achieved, and higher rates may be possible. The process does not appear to have potential for multipollutant removal. Secondary pollution could result from disposal of the gypsum product if it cannot be sold. This gypsum, however, should be of much higher quality than the calcium sulfite/sulfate sludge produced by conventional lime/limestone processes. Energy requirements would be slightly lower than those for the lime/limestone processes. The stack gas must be reheated from saturation, L/G would be relatively high and pressure drop moderate. Lime, magnesium hydroxide, and possibly sulfuric acid are required as raw materials.

Development Status - Kawasaki Heavy Industries has constructed two commercial plants (equivalent to approximately 67 and 73 MW) using the magnesium-gypsum process. The plants went into operation in early 1976, treating the flue gas from oil-fired boilers. All process steps were integrated at these plants. The process uses currently commercialized technology. Minor scale-up problems could be experienced.

Economic and Technological Considerations - This process is slightly more complex, both chemically and mechanically, than conventional lime/limestone or sodium double alkali processes. Scale formation was a problem in early operation of the process, but apparently has been eliminated by proper process control. The magnesium could have an adverse effect in solids properties, leading to potential problems with producing a salable gypsum.

Applicability - This process appears to be generally applicable for utility and industrial applications. It can be turned down, retrofitted, and modularized. Process sections can be decoupled. Applicability is somewhat limited by the need to sell or dispose of large quantities of gypsum which, although more easily handled than sludge, nevertheless requires land for disposal if the product cannot be sold.

Summary and Conclusions - This process scored relatively high compared to other throwaway processes. It is well developed and has good applicability, but scored average ratings in the categories of Environmental and Energy Considerations and Economic and Technological Considerations. It utilizes a simple scrubber and should be capable of better SO_2 removal than lime scrubbing, due to the addition of magnesium, but the supporting reactions are more complex. Gypsum is produced as a by-product rather than $CaSO_3/CaSO_4$ sludge. It is recommended that this process concept be considered as an alternative to conventional lime scrubbing.

Reference - AN-147

KIYOURA-TIT PROCESS

Process/Subsystem Description - The Kiyoura-TIT Process involves catalytic oxidation of SO_2 to SO_3 at a high temperature in a process similar to that used in contact-type sulfuric acid plants. Rather than absorbing the SO_3 by condensing moisture from the gas, however, ammonia is added (at a point where the gas temperature is above the H_2SO_4 dew point) to form $(NH_4)_2SO_4$ in the gas stream. This $(NH_4)_2SO_4$ is collected in dust collection equipment such as an electrostatic precipitator.

Environmental and Energy Considerations - The process has achieved SO_2 removal efficiency of slightly more than 90%. (Conversion efficiency was 93%, and $(NH_4)_2SO_4$ collection efficiency 97.5%). Other pollutants are not captured by the system. Particulate removal is necessary before and after the oxidation step. $(NH_4)_2SO_4$ particles not picked up in the product collection equipment are released to the atmosphere, presenting a potential secondary pollution problem. Unreacted ammonia may also escape in the stack gas. Energy requirements will be greater for a retrofit application since the flue gas may have to be reheated to catalyst temperature. Two electrostatic precipitators may be required for preliminary dust removal and product recovery. No exit gas reheat will be required. The principal raw material required is ammonia; some makeup catalyst will also be needed. Both should be readily available.

Development Status - The process was tested in 1967 at a small pilot plant cleaning gas from an oil-fired boiler. The oxidation step uses technology developed from the sulfuric acid manufacturing industry, and no serious scale-up problems are apparent. No further work is known to have been done on the process since the initial pilot plant tests, however.

Economic and Technological Considerations - Poisoning or plugging of the catalyst could be a problem. Variations in temperature and in SO_2 and O_2 concentrations in the flue gas also complicate the oxidation step. In addition, two sets of particulate collection equipment are required; one to remove dust prior to oxidation and one to collect the $(NH_4)_2SO_4$ particles.

Applicability - Certain species in the boiler fuel, such as fluorine or chlorine, contribute to catalyst deactivation. Ammonium sulfate is produced as a by-product. Retrofits would be difficult, since the flue gas may have to be heated up to catalyst temperature. The process cannot be decoupled.

Summary and Conclusions - Development of the Kiyoura-TIT Process ceased in 1967. This appears to be due mainly to insurmountable problems with secondary pollution by ammonium sulfate and overall complexity of the system. In addition, the process is only applicable in those areas where ammonium sulfate has a ready market. These problems combined to give the process a relatively low score and, therefore, it should not be evaluated further.

References - SL-070

KOYO PROCESS

Process/Subsystem Description - In this process, developed by the Koyo Iron Works in Japan, an aqueous solution of NaOH and Na_2CO_3 is atomized and sprayed into flue gases in a spray dryer. The SO_2 reacts to form Na_2SO_3 and some Na_2SO_4. The solution water is dried by the heat of the flue gases so that a powdered solid mixture of Na_2SO_3, Na_2SO_4, and unreacted Na_2CO_3 is produced. The dry product is collected by multicyclones and an electrostatic precipitator.

Environmental and Energy Considerations - SO_2 removal efficiencies of 80-90% are claimed. No other pollutants are removed. Severe secondary pollution problems could result from carryover of NaOH into the stack gas or from disposal of Na_2SO_3. (The Na_2SO_3 may have use in the Kraft pulping process, however.) Energy requirements should be relatively low, reheat may not be required, no reducing gas is needed, and L/G and pressure drop should be quite low. The raw materials required are Na_2CO_3 and NaOH.

Development Status - The absorption and product collection steps are quite similar to those in the Atomics International Aqueous Carbonate Process, but the Koyo process involves selling or discarding the sodium sulfite/sulfate rather than regenerating it. Apparently the Koyo process has not been tested on a coal-fired boiler, but is reportedly undergoing a large-scale test at an oil-fired boiler at a pulp mill. The process has been integrated. It uses commercial technology to an extent, but the use of a spray dryer for SO_2 scrubbing is not considered commercial technology. Some scale-up problems are expected for scale-up of the spray dryer.

Economic and Technological Considerations - The process is basically simple chemically but quite complex mechanically. Efficient atomization of the scrubbing solution is essential for good SO_2 removal. Control of scrubbing solution concentration is also important. A sufficient quantity of Na_2CO_3 and NaOH to react with the incoming SO_2 must be provided. The amount of water used to dilute the scrubbing solution must be limited to insure a dry product, but a sufficient quantity of dilution water must be added to provide the gas/liquid contact area needed for the desired SO_2 removal.

Applicability - The process appears applicable to both industrial and utility situations. However, utility applicability may be hindered by its mechanical complexity. The process may be modularized and there is no regeneration step. Turndown of the spray dryer may be difficult, and retrofitting the spray dryer into utility boilers may be difficult because of space limitations. Applicability is further limited to areas where a plentiful supply of sodium carbonate is available, and where the sodium sulfite/sulfate product can be marketed or disposed of safely.

Summary and Conclusions - This process rates relatively low compared to other throwaway processes. SO_2 removal is not as good as that achieved with conventional Na_2CO_3 scrubbing, but better than that attainable with fabric filters. The Koyo process is more complex mechanically than fabric filters. Additional particulate removal is required following the spray dryer. Applicability is limited to areas where a cheap, plentiful supply of sodium carbonate is available. Because of the expense of the sodium carbonate, the process is also limited to applications with low or moderate sulfur coal. Since this process is more complex and offers no real advantages over aqueous Na_2CO_3 scrubbing it should not be considered further.

References - CA-327

KREBBS-NEVILLE PROCESS

Process/Subsystem Description - The Krebs-Neville process is a version of the NaOH/Ca(OH)$_2$ double alkali system which is modified by the addition of a proprietary catalyst to the scrubbing medium to promote NO$_x$ removal. The catalyst complexes the NO$_x$ in solution long enough for it to be reduced to N$_2$ and/or N$_2$O by the sulfite and bisulfite in the solution. NO$_x$ removal of 70% has been claimed for an NO$_2$:NO ratio of 30:70.

Environmental and Energy Considerations - NO$_x$ removal capabilities have been claimed, but removal would require ozonation to achieve the necessary NO$_2$:NO ratio. Other considerations would be similar to those of the current double alkali technology.

Development Status - The process reportedly has been piloted at the 750 acfm level. However, the process has been dropped as being impractical and has been dormant for several years.

Economic and Technological Considerations - The process offers no advantages over the current double alkali technology other than possible NO$_x$ removal. The NO$_x$ removal feature would probably require ozonation, which has high capital equipment and energy costs. From this standpoint the process shows no advantage over Japanese ozonation-based processes which are more fully developed.

Applicability - Without the addition of an ozonation step, the process is not applicable as both an SO$_2$ and NO$_x$ removal system since normal flue gas contains a much too low NO$_2$:NO ratio.

Summary and Conclusions - This process claims NO$_x$ removal, but would probably require ozonation to achieve it. NO$_x$ removal would also be complicated by high oxidation rates. Not enough information was available to evaluate the process adequately; therefore, it is not recommended for further consideration.

References - CH-405

KURABO

Process/Subsystem Description - SO_2 is absorbed in an ammonium sulfite solution at pH 3-4 with forced oxidation in the scrubber loop. A slipstream is neutralized with lime to give a gypsum product and aqueous NH_3 which is recycled to the scrubber loop. Alternatively, ammonium sulfate solution from the scrubber can be marketed as fertilizer.

Environmental and Energy Considerations - An SO_2 removal efficiency of more than 90% has been achieved. The process does not appear to have potential for multipollutant removal. Secondary pollution problems could result from disposal of the gypsum product. Ammonia plume formation is not a problem with this process as it is for other ammonia scrubbing processes because of the low pH of the scrubbing solution. Energy requirements may be slightly higher than those for the sodium double alkali process. Reheat will be required, and L/G and pressure drop are relatively high. Ammonia and lime are required as raw materials.

Development Status - This process has been demonstrated commercially on oil-fired boilers in Japan. It has been fully integrated. Current technology is used. No scale-up problems are anticipated.

Economic and Technological Considerations - This process has about the same degree of chemical and mechanical complexity as the sodium/lime double alkali process. The process is suitable for any level of scrubber oxidation. Chloride buildup will require purging as $CaCl_2$ or NH_4Cl solution. A countercurrent scrubber is required for good SO_2 removal (>80%). (Use of an organic acid additive would eliminate this constraint on scrubber design.) Volatility of ammonia may present on-site problems in the regeneration step. Adequate containment or venting is required.

Applicability - This process appears to be generally applicable for utility or industrial use. It can be turned down, retrofitted, and modularized. Process sections can be decoupled. Applicability is limited by the need to sell or dispose of large quantities of gypsum or ammonium sulfate, but the flexibility to produce either gypsum or ammonium sulfate is attractive. The market for ammonium sulfate is probably limited, but may be sufficient in specific, local instances. If it is necessary to dispose of the gypsum, although it is more easily handled than sludge, it nevertheless requires land for disposal.

Summary and Conclusions - This process scored well above average compared to other throwaway processes. It is well developed, has good applicability, and scored slightly above average in Environmental and Energy Considerations and as high as any throwaway process in Economic and Technological Considerations. It is superior to all other ammonia scrubbing processes because the low pH suppresses fume formation. It has advantages over the sodium/lime double alkali process because it can tolerate any level of scrubber oxidation and produces a gypsum product rather than calcium sulfite/sulfate sludge. It requires a relatively high L/G, however, and must use lime rather than limestone for regeneration. This process is recommended for further evaluation.

References - AN-147, YO-058

KUREHA (SO_2/NO_x)

Process/Subsystem Description - The Kureha Process uses a sodium sulfite-acetic acid solution to absorb SO_2 and NO_x. Absoprtion of NO_x is aided by a catalyst in the absorbing liquor. Vaporized acetic acid is recovered by ammonia scrubbing in the second compartment of a two-compartment absorber. The flue gas is prescrubbed for particulate and chloride removal before it is passed through the absorbers for SO_2 and NO_x removal and acetic acid recovery. A limestone slurry is used to regenerate the acetic acid and produce a gypsum by-product. Sodium imidodisulfanate formed in the absorber by absorption of NO_x is ultimately decomposed to N_2 in several steps including hydrolysis with addition of H_2SO_4 to produce NH_4HSO_4, reaction of NH_4HSO_4 with lime to produce NH_3, and catalytic oxidation of NH_3 to N_2.

Environmental and Energy Considerations - Testing of a pilot plant unit firing heavy oil demonstrated 99% SO_2 removal and 80-90% NO_x removal. Particulates and chlorides are also removed. There is a possibility of ammonia emissions from the absorber, however, and disposal of the gypsum by-product may pose an additional environmental problem. Reheat is required, but reducing gas is not. The L/G ratio in the first section of the absorber is high; 125-185 gal/Macf. The second stage operates with an L/G of 12.5 gal/Macf. Raw materials required are calcium hydroxide, sulfuric acid, catalyst, acetic acid, and sodium hydroxide.

Development Status - The Kureha Process has not been tested on flue gas from a coal-fired boiler. It was developed as a modification to the original sodium acetate/gypsum flue gas desulfurization process. The integrated process has been tested at the pilot plant level on flue gas from an oil-fired boiler. Commercialized technology is used throughout the process with the possible exception of the two stage absorber. Scale-up may present a problem because the process has not been tested on coal-generated flue gas.

Economic and Technological Considerations - This process is complex when compared to other flue gas desulfurization processes, but it is simpler than some of the other NO_x/SO_2 removal processes. The workability of the process on coal-fired units remains to be demonstrated. Large absorbers are required for removal of NO_x. Polymer-lined carbon steel will be used for most of the equipment, but some portions will be made of Inconel 625 and glass-lined steel.

Applicability - The Kureha Process is potentially applicable to industrial and utility installations if sufficient land area is available. Decoupling would be difficult due to the large volumes of storage required. Retrofit is judged easy, and load following capabilities should be good. By-product gypsum will probably have to be landfilled.

Summary and Conclusions - Advantages to this process include high SO_2 removal and simultaneous NO_x removal. It has disadvantages, however, in its complexity when compared to FGD systems, its high L/G ratio, its requirement for flue gas reheat, and its lack of testing on coal-generated flue gas. It is not recommended for further consideration.

References - FA-149.

KUREHA SODIUM ACETATE

Process/Subsystem Description - SO_2 is absorbed in a slurry of gypsum in sodium acetate/sulfate solution. Bisulfite is oxidized to sulfate by an air oxidizer in the scrubber loop. A slipstream is neutralized by CaO or $CaCO_3$ to produce gypsum. The scrubber includes a top section of CaO or $CaCO_3$ slurry scrubbing to recover volatilized acetic acid. The process differs from Dowa in that acetate buffer rather than $Al_2(SO_4)_3$ is used, and by recycling gypsum solids to the scrubber.

Environmental and Energy Considerations - This process is capable of achieving excellent SO_2 removal (99%) and has potential for removing NO_x as well. Secondary pollution problems could result from disposal of the gypsum if it cannot be sold. Energy requirements are comparable to those for a double alkali process. Gas reheat is required, but pressure drop and L/G should be relatively low. Acetic acid, sodium hydroxide, and lime or limestone are required as raw materials.

Development Status - The process has been tested by Kureha in Japan at a 2500 cfm oil-fired pilot plant. It has also been tested at the bench scale (60 cfm) on flue gas from a coal-fired boiler, but it is not offered in the U.S. The process has been fully integrated. Current technology is used. Some scale-up problems may be experienced.

Economic and Technological Considerations - This process is more complex, chemically and mechanically, than the sodium/lime double alkali process. The volatility of acetic acid complicates scrubber design. Slurry scrubbing (with $CaSO_4$ solids) seems to be required to prevent gypsum scaling. The process is suitable for any level of oxidation, however, acetic acid makeup is minimized by washing the gypsum product.

Applicability - This process appears to be generally applicable to utility or industrial applications. It can be turned down, retrofitted, and modularized. Process sections can be decoupled. Applicability is limited by the need to sell or dispose of large quantities of gypsum. Although gypsum is more easily handled than sludge, it nevertheless requires land for disposal if it cannot be sold.

Summary and Conclusions - This process scored slightly above average compared to other throwaway processes. It has good applicability, and it scored well in Environmental and Energy Considerations because of its ability to achieve excellent SO_2 removal at a relatively low L/G. The acetate buffer necessitates more complicated scrubber design, however, and the process is not as well developed as some of the other throwaway processes. Slurry scrubbing with a nonvolatile buffer such as adipic acid may be preferable. This process is not recommended for further consideration.

References - SA-236

LEAD-ZINC ORE PROCESS

Process/Subsystem Description - Laboratory studies by the Bureau of Mines involved passing simulated flue gas through a bed of lead-zinc ore tailings, which consist primarily of dolomite carbonates. High removal rates required reactor temperatures between 930-1110°F. Attempts at direct injection of the tailings into a small pulverized coal-fired furnace yielded a maximum SO_2 removal efficiency of less than 30%. Results of a comparison with limestone showed the tailings to have roughly half the absorbing capacity of an equivalent amount of limestone.

Environmental and Energy Considerations - Low SO_2 removal efficiencies would probably be achieved with this process. No other pollutants appear to be removed from the flue gas, but the raw material used for SO_2 absorption is a waste mineral. Because of the low absorptive capacity of the sorbent (about half that of limestone), a large quantity of SO_2 absorption products are generated. Disposal of these wastes could cause serious secondary pollution problems. Energy requirements should be relatively low; gas preheat may be required and L/G and pressure drop should be relatively low.

Development Status - The process has been evaluated only at the laboratory scale and apparently has not been integrated. Current technology is used, but serious scale-up problems are anticipated.

Economic and Technicological Considerations - The process appears to be quite complex, both chemically and mechanically. In addition, although the sorbent is quite cheap (less than $20 per ton), the high temperatures required and the large amount of waste material produced make the process unattractive.

Applicability - The high reaction temperatures required make it necessary to locate the absorber near the source of hot flue gas, limiting retrofit applicability. Modularization may also be difficult, but turndown and decoupling ability should be acceptable. Applicability is further limited to areas where a supply of lead-zinc ore tailings is available and where the large quantities of waste products may be disposed of.

Summary and Conclusions - This process scored well below average compared to other throwaway processes in all four evaluation categories. It has the advantage of using a waste product as a raw material, but generates very large quantities of waste products from the SO_2 absorption. The process may not be capable of achieving adequate SO_2 removal, and is limited to areas where a source of the lead-zinc ore tailings is available. This process is not recommended for further evaluation.

Reference - HA-654

LEWIS PROCESS

Process/Subsystem Description - The Lewis Process is a modification of the conventional lime scrubbing process. The usual scrubber and separate lime slaker are replaced by a rotary drum scrubber, which visually resembles a rotary kiln. The scrubber has flights and series of transverse chains (fixed at either end of the drum), which lift lime slurry to the top of the scrubber and allow it to cascade through the axial flow of the flue gas. In addition to serving as mobile packing, the chains prevent plugging and remove scale from the scrubber walls. Other claimed advantages for the rotary drum scrubber include: 1) lower pressure drop than most lime scrubbers; 2) mist removal by the chains; 3) low pumping power requirements; and 4) suitability of carbon steel construction.

Environmental and Energy Considerations - It is doubtful that the chains in the rotary drum scrubber provide as good a mass transfer medium as other types of packing currently being used. Fly ash and SO_2 removal efficiencies are not likely to be as high as for other scrubbers, and the mist removal claims require substantiation. The secondary pollutant problems are identical to those for conventional lime/limestone systems: a $CaSO_4/CaSO_3$ sludge is produced. Stack reheat is needed, but the system pressure drop is less than for the conventional process.

Development Status - The Lewis Process has been developed to the pilot scale, but no information was found concerning the size or the source of flue gas (oil or coal). The degree of integration was not stated, but by-product treatment and disposal should be identical to other lime scrubbing systems. An industrial application was planned as of 1975.

Economic and Technological Considerations - The Lewis Process is well-defined chemically. Although the rotary drum scrubber is relatively simple, there may be attrition problems with the chains. The scrubber has not been used in a full-scale FGD application, but scale-up should not be very difficult.

Applicability - Like the conventional lime scrubbing processes, the Lewis Process should have good potential for turndown and retrofit applications. Sludge disposal is a problem and the system cannot be decoupled.

Summary and Conclusions - Because the scaling problems previously observed in lime/limestone scrubbing systems have been resolved in newer installations, there appears to be no major advantage of the Lewis Process over the commercially available systems. In addition, there is some doubt concerning the effectiveness of the fly ash and SO_2 removal in the rotary scrubber. The process is not recommended for further evaluation.

Reference - SL-070

LURIE SODIUM ALUMINATE PROCESS

Process/Subsystem Description - $Na_2Al_2O_4$ and NaOH contact flue gas in a packed bed to produce Na_2SO_4 and $Al_2(SO_4)_3$. The salts are mixed with carbonaceous material and evaporated to dryness, evolving SO_2 and forming a mixture of carbon and $NaAL(SO_4)_2 \cdot 12H_2O$. The dry salt reacts with carbon at 1800°F to produce molten Na_2S and Al_2S_3. The sulfides are quenched and hydrolyzed to form gaseous H_2S as well as $Al(OH)_3$ and NaOH, which immediately react to form $Na_2Al_2O_4$. The $Na_2Al_2O_4$ is filtered and returned to the absorber. The H_2S, along with the SO_2 from the evaporation step, can be sent to a Claus plant for sulfur production.

Environmental and Energy Considerations - This process should be capable of effective SO_2 removal. No other pollutants appear to be removed. There should be no serious secondary pollution problems, although a purge stream could be necessary to remove chlorides and other trace contaminants. L/G and pressure drop should be relatively low. Reheat will be required. A reducing gas is not required for the regeneration step, but a source of carbon is. Carbon, NaOH, and possibly makeup aluminum appear to be the only raw materials required.

Development Status - The process has been tested at the laboratory scale with air-diluted SO_2. The process apparently requires extensive use of noncurrent technology, but the process is quite similar to the Atomic's International Aqueous Carbonate Process. Extensive scale-up problems may be experienced.

Economic and Technological Considerations - The process has several steps that will involve chemical or mechanical complexities. These steps include reduction in a molten salt pool and filtration of ash. Special materials of construction would be required for the reducer, which must contain molten salts at a high temperature. Formation of $Al(OH)_3$ gel could cause severe operating problems.

Applicability - This process appears to be generally applicable for utility or industrial use. It apparently could be turned down, retrofitted, and modularized. Process sections can be decoupled. The H_2S and SO_2 that are evolved are sent to a Claus plant to produce elemental sulfur. Thus, by-product marketability should not limit applicability.

Summary and Conclusions - This process scored relatively low compared to other wet regenerable processes because of its low development status and chemical and mechanical complexity. The process is similar to the Atomics International Aqueous Carbonate Process (ACP), but appears to have several advantages. The sorbent is reformed directly after the quench step without the carbonation step required by the ACP. Greater sorbent capacity is another advantage; one mole of $Na_2Al_2O_4$ picks up 4 moles of sulfur so that the weight ratio is much lower than that for Na_2SO_3 or Na_2CO_3. Evolution of SO_2 during evaporation, however, adds a complexity not found in the ACP, and the formation of $Al(OH)_3$ gel could cause severe operating problems. This process is not recommended for further evaluation.

References - PL-045, CH-401

MAGET PROCESS

Process/Subsystem Description - An acidic carbon slurry is used to sorb SO_2. The carbon slurry, with the sorbed SO_2, is pumped to an electrochemical cell where the SO_2 is oxidized to H_2SO_4, with simultaneous production of hydrogen. The slurry is separated from the H_2SO_4 in a settling tank and is recycled, while the acid is transferred to a concentrator.

Environmental and Energy Considerations - High SO_2 removal rates are claimed. NO_x and hydrocarbon removal capability is claimed, but is questionable since these species must be transferred to the acidic liquor before they can be absorbed by the carbon. Energy requirements may be large because of the very high liquid rates that must be circulated to achieve high SO_2 removal. Electricity is also required in the process regeneration steps, and stack gas reheat will be required. The only process raw material is activated carbon.

Development Status - The process is essentially in a conceptual development stage. The use of standard equipment is claimed but the equipment would be subjected to untried operating conditions. Solids handling problems would have to be resolved before the process could be scaled-up.

Economic and Technological Considerations - The process will be very complex mechanically to deal with solids handling problems. The chemistry of the process in the slurry electrolytic cell is also a complex and unproven process.

Applicability - There appear to be no fuel constraints. Construction materials to handle the warm, aerated, acidic stream would be expensive. A dilute acid is produced and must be concentrated. Retrofit could be limited by land requirements. Turn down is relatively easily accomplished but the process cannot be decoupled.

Summary and Conclusions - The process offers no apparent economic, technological, or energy saving advantages over the more developed dry adsorption processes. This coupled with its conceptual development status lead to the conclusion that the process should not be considered further.

References - MA-699, MA-700

MASS TRANSFER ADDITIVES WITH LIME/LIMESTONE SCRUBBING

Process/Subsystem Description - Various additives can be used with conventional lime or limestone scrubbing processes to enhance mass transfer, thus improving SO_2 removal, increasing limestone utilization, and permitting the use of simple scrubber types (such as cocurrent scrubbers). Possible additives include alkali additives, such as MgO, Na_2CO_3, and NH_3, and organic acids, such as adipic, acrylic, or glycolic acids.

Environmental and Energy Considerations - SO_2 removal efficiencies greater than 90% would be possible in lime or limestone systems with addition of the additives. Additive addition does not enhance multipollutant removal capability. Additive losses with waste solids could be a significant economic and environmental problem. Solids handling procedures will significantly affect costs for makeup additives.

Alkali additives contribute total dissolved solids to the scrubbing liquor, and organic acids contribute biochemical or chemical oxygen demand (BOD or COD), intensifying waste disposal problems. In addition, volatility and toxicity can be problems with certain additives. Energy requirements for lime or limestone processes with additives are comparable to those for a system without additives. No reducing gas is required, but gas reheat is required. In general, the proposed additives should be readily available.

Development Status - The use of magnesium as an additive has been tested extensively. In Japan, two units (approximately 70 Mw equivalent each) using a process developed by Kawasaki-Heavy Industries were put into operation in oil-fired boilers in January, 1976. The process consists of lime slurry scrubbing with addition of MgO, and also uses forced oxidation. Pullman Kellogg Co. offers a limestone scrubbing process with MgO addition. Benzoic acid has been tested at the pilot plant level by TVA. Other additives have not been tested extensively. Additives can, however, be tested, developed, and demonstrated in existing equipment. Thus, commercial technology is used in all process sections, and there should be no scale-up problems.

Economic and Technological Considerations - In general, the use of additives should improve operability of limestone scrubbing systems. Limestone utilization can be improved. The potential for mist eliminator plugging can be decreased due to increased lime/limestone utilization. Because of the improved mass transfer, simple scrubber types can be used to achieve good SO_2 removal. Use of alkali additives may not be desirable in systems saturated with calcium sulfate, however, since they can contribute to scaling. Alkali additives may not be attractive in systems burning high chloride coals since sufficient alkali must be added to balance the chlorides before an excess is available for mass transfer improvement. In addition, magnesium can affect gypsum crystallization. These constraints do not apply to the organic additives, however. The mass transfer additives affect liquid phase mass transfer resistance and thus are generally less effective with low sulfur coals, where gas phase resistance controls. Use of additives will complicate solids disposal practices since care must be exercised to minimize additive losses.

Applicability - Use of additives should not significantly affect applicability of conventional lime/limestone systems.

Summary - The use of mass transfer additives appears to be a promising method for improving the SO_2 removal capability of lime or limestone slurry scrubbing processes. Economic and environmental effects of additive losses with waste solids are a potential disadvantage, but such losses can be minimized by the use of forced oxidation to decrease the water content of the waste solids. More research is needed to determine the most promising additives and to quantify the optimum addition rates. Additives can be tested, developed, and demonstrated in existing equipment. The use of additives will be considered further as an alternative in lime/limestone scrubbing.

References - AN-147, RO-333, RO-313

MCKEE MODIFICATION OF CITRATE PROCESS

Process/Subsystem Description - The SO_2 absorption and absorbent regeneration steps of this process are identical to the conventional BOM Citrate Process: 1) SO_2 is absorbed from flue gas by a citric acid/sodium citrate buffer solution; and 2) the sorbent is regenerated and sulfur is produced by reduction of the absorbed SO_2. In the conventional process, the reduction is accomplished using H_2S, which is produced by reaction of some of the product sulfur with steam and natural gas. The McKee Modification is based on the assumption that the active agent in the SO_2 reduction step is not H_2S, but hydrosulfide ion, HS^-. For production of HS^- (and some H_2S), McKee proposes that a side stream of SO_2-rich absorbent be slurried with CaS in a reactor/clarifier. The overflow (containing NaHS) is returned to the regeneration reactors while the underflow (precipitated $CaSO_4$ and $CaSO_3$) is dewatered and reduced back to CaS by reaction with coke in a kiln.

Environmental and Energy Considerations - The McKee Modification should not affect the excellent SO_2 removal shown by the conventional Citrate Process. The potential for multiple pollutant removal remains poor, but the Na_2SO_4 purge required by the BOM process is eliminated by the $CaSO_4$ reduction step. Although operation of the reduction kiln requires both energy and a raw material (coke), the need for natural gas is eliminated, and this is a favorable trade-off. Stack reheat requirements and absorber pressure drop are comparable to other wet FGD processes.

Development Status - The absorption and regeneration steps have been well tested by BOM at the pilot scale with coal. However, no test work at all has been performed using hydrosulfide ion as the reductant for the regeneration step. The reduction of $CaSO_4$/$CaSO_3$ is a commercially used process for CaS production. The McKee Modification could readily be tested as an add-on to the Citrate Process demonstration unit currently under construction if bench scale tests of the concept are successful.

Economic and Technological Considerations - The McKee Modification does not appear to add to the chemical or mechanical complexity of the basic Citrate Process, but the concept has not been tested even on the bench scale. Successful development of the modification will hinge on the ability to use hydrosulfide as the reductant in the sorbent regeneration step. McKee points out several similarities between the Citrate Process with their modification and the Mag-Ox Process, and they feel the costs should be similar.

Applicability - The citrate modification suffers from the same poor turndown as the parent process because of the need for balancing of the absorber inlet SO_2 rate and the sorbent regeneration rate. However, because CaS (unlike H_2S) can be easily stockpiled, the reductant generation step can be decoupled from the remainder of the process.

Summary and Conclusions - The McKee Modification is conceptual, so it cannot readily be evaluated objectively. It has a major advantage over the conventional Citrate Process in that it does not require a reducing gas. Because the concept can be readily tested at the citrate demonstration unit now being constructed, the McKee Process Modification is recommended for further consideration as a process alternative to the Citrate Process.

References - MC-321.

MELAMINE PROCESS

Process/Subsystem Description - This process involves SO_2 scrubbing by melamine slurry followed by a thermal regeneration step. After treatment in a venturi prescrubber for fly ash and chloride removal, gas is scrubbed by the melamine ($C_3H_6N_6$) slurry in a two-stage countercurrent spray tower. The slurry is then filtered and the liquor returned to a reslurry/recycle tank. The solid mixture of sulfites and sulfates is fed to a two-stage fluid bed dryer. The first stage is for removal of water of hydration. The second stage, which is operated at 392°F, is a thermal decomposition step producing a mixture of melamine solids, SO_2, and water. The water is condensed and the SO_2 is sent to an acid plant. The melamine solids, which contain melamine and melamine sulfate, are split into two streams, with two-thirds returning to the reslurry/recycle tank and one-third going to a chemical decomposition step for removal of thermally nonregenerable melamine sulfate. In this step, melamine sulfate is reacted with ammonium hydroxide to form soluble ammonium sulfate and melamine solids. The solids are filtered and recycled and the ammonium sulfate is recovered as a by-product.

Environmental and Energy Considerations - SO_2 removal of greater than 99% is reported. The system offers no multipollutant removal capabilities. Energy requirements for the system should be similar to those of the magnesia slurry process except in the regeneration area where energy consumption should be lower due to lower temperatures. Scrubber pressure drop should be relatively low, but gas reheat will be required. Raw materials required include melamine, ammonium hydroxide, and a special antioxidant for control of sulfate production.

Development Status - The process has been demonstrated at bench scale, including glassware tests on flue gas from a coal-fired source. The process has not been fully integrated. It uses commercialized technology except for the use of the fluid bed dryer. Scale-up capabilities are questionable at this time due to the limited development status.

Economical Technological Considerations - The process is mechanically complex, on the same order of complexity as the magnesia slurry process. However, the requirement of adding a separate chemical decomposition step for sulfate removal adds some chemical complexity beyond that of the magnesia slurry process. For this reason, costs will probably be higher than those of the magnesia slurry process.

Applicability - The process should present no major problems for turndown capability or retrofit. The addition of storage facilities could make both decoupling and centralized regeneration possible.

Summary and Conclusions - The Melamine process rated above average among the wet regenerable FGD processes. It was penalized because of its limited development status and its mechanical complexity. This process is recommended for further evaluation due to its potential for improving the process concept employed by the magnesia slurry process.

Reference - MC-322

MIKROPUL WET ELECTRIC PRECIPITATOR PROCESS

Process/Subsystem Description - The Mikropul process is a conventional wet scrubbing, throwaway process, except that a wet electrostatic precipitator (WEP) is used as the contactor for SO_2 removal. Prior to entering the WEP, the flue gases are cooled and humidified by water sprays. Absorbing solution (several have been tested) is then sprayed into the gas stream, both in a pretreatment section of the WEP and between the discharge/collector electrode pairs within each precipitator stage. The spray droplets (containing absorbed SO_2) and fly ash are charged and collected conventionally. The collected material flows down the collectors to a sump from which it is drained to an effluent treatment area. The nature of the treatment is dependent on the absorbent being used.

Environmental and Energy Considerations - Laboratory scale tests of the Mikropul Process have shown SO_2 removal efficiencies ranging from 62% to 99%, depending on the choice of absorbent. As would be expected, the more basic materials (caustic and soda ash solutions) yielded the higher efficiencies. There may be some potential for NO_x removal, but none is claimed. The other environmental impacts of the process depend on the absorbent used, but fly ash contamination of the by-product will complicate matters where the material has some market value (for example sodium sulfate). The cleaned flue gases may require reheat, but the process has a very low pressure drop in comparison with other wet scrubbing systems. ESP power consumption is relatively low.

Development Status - The Mikropul Process has been tested only on a laboratory scale, using simulated flue gases. The treatment of the by-product stream from the WEP has not been studied in any detail, particularly the fly ash contamination, if soluble sulfates/sulfites are the by-products.

Economic and Technological Considerations - The WEP Process is based primarily on existing technology and is relatively simple from both a chemical and a mechanical point of view. Capital and operating costs for the process are uncertain at this time. The developer has addressed only costs associated with the electrostatic precipitators and not those associated with product treatment and disposal to date. Other than the low pressure drop across the scrubber and excellent fly ash removal, this process does not appear to offer any significant advantages over more highly developed wet scrubbing processes.

Applicability - This process would be expected to show excellent turndown capability for all applications. Retrofit potential is poor because of space requirements and/or the possible duplication of existing fly ash removal equipment. The wet precipitator requires a continuous flow of absorbent, and it cannot be decoupled from the absorbent preparation area. Loss of absorbent flow results in loss of both SO_2 and fly ash control. The marketability of the by-products is considered poor.

Summary and Conclusions - The Mikropul WEP Process for FGD appears to be feasible, but it offers no significant advantages over commercially available processes such as lime or limestone throwaway processes. When using lime the WEP Process shows considerably poorer SO_2 removal efficiency (62-70%) than conventional lime processes. Consequently, the process should not be further evaluated.

References - MI-293

MITSUBISHI HEAVY INDUSTRIES

Process/Subsystem Description - In the Mitsubishi Heavy Industries process flue gas is prescrubbed for cooling and ozone is used to oxidize nitric oxide to nitrogen dioxide and SO_2 to SO_3 prior to entering the absorber. The SO_3 and NO_2 in the flue gas are then absorbed by a lime or limestone slurry containing a water soluble catalyst which aids in the absorption of the NO_2. The flue gas is reheated, and exhausted from the stack. The nitrogen oxides are removed as ammonia, and the SO_3 is removed as gypsum.

Environmental and Energy Considerations - A pilot plant unit treating oil-fired flue gas has achieved 95% SO_2 removal and 80-90% NO_x removal. The prescrubber removes particulates and chlorides. Disposal of by-product gypsum poses a potential environmental problem. There is an ammonia off-gas which will have to be treated to avoid its release into the environment. Energy requirements include reheat of the flue gas. There is no requirement for reducing gas; however, ozone is required, and ozone generation is very energy intensive. The L/G ratio in the absorber is a little lower than some of the other SO_x/NO_x systems (44-62 gal/Mcf). Raw materials required are limestone, slaked lime, sulfuric acid, and catalyst.

Development Status - This process has not been tested on flue gas from a coal-fired boiler. Pilot plant testing has been performed on oil-generated flue gas. The method of ammonia removal has not been determined, however. Commercially available technology is used in most of the process. Scale-up problems may be encountered as a result of not having tested the process on coal-generated gas. Also, the ammonia removal method has not been specified, so that scale-up problems may also exist in that section.

Economic and Technological Considerations - The Mitsubishi Heavy Industries Process is less complex than some of the other SO_x/NO_x removal processes. It is more complex than conventional limestone FGD processes. The workability of the process on coal-generated flue gas remains to be determined. Most of the equipment will be polymer-lined carbon steel. Some of the equipment will be made of Inconel 625, stainless steel, or glass-lined steel.

Applicability - This process may be useful for industrial and utility applications. Retrofit is judged easy if sufficient space is available. Decoupling should also be possible although large storage volume is required. Load following capabilities should be good. The by-product gypsum will probably not be marketable in the U.S. Ammonia would probably be a marketable by-product although the quality has not been specified at this time.

Summary and Conclusions - The Mitsubishi Heavy Industries Process was rated below average. The simultaneous removal of NO_x and SO_2 adds complexity to the process compared to the conventional flue gas desulfurization systems. It has not been tested on coal-generated flue gas. Further, it requires ozone generation as well as flue gas reheat. The ammonia off-gas may present an environmental problem, and the gypsum will probably have to be landfilled. The process is not recommended for further consideration.

References - (TVA) FA-149

MITSUBISHI MANGANESE OXIDE

Process/Subsystem Description - Hot flue gases are contacted with manganese oxide in an entrained reactor with the removal of SO_2 and the formation of manganese sulfate. The entrained manganese sulfate is removed by cyclones and electrostatic precipitators and the gas vented to the stack. The dry manganese sulfate is slurried in water and reacted with ammonia, producing manganese hydroxide and ammonium sulfate. The manganese hydroxide is then oxidized to manganese oxide in an air oxidation tower. The slurry is filtered and the damp manganese oxide cake is returned to the scrubber. The ammonium sulfate filtrate is crystallized and utilized in the manufacture of fertilizer.

Environmental and Energy Considerations - This process has a 90% SO_2 removal efficiency and produces ammonium sulfate which can be used as a fertilizer. NO_x or other pollutant removal has not been experienced. Although reheat of the flue gas is not required the process would require energy for operation of the ESP, air compressor, process pumps and ammonium sulfate purification dryers, heaters and centrifuges. Raw materials required include manganese oxide and ammonia, both of which should be readily obtainable. Secondary pollution with manganese oxide escaping out the stack is a serious problem. Manganese sulfate emission has been experienced and this compound presents a serious public health hazard.

Development Status - A large amount of experimentation has taken place with the concept of manganese oxide absorption. The Mitsubishi Process was demonstrated on an oil-fired plant generating approximately 500,000 lb/hour of steam. Operation of the unit was discontinued in 1967 due principally to manganese compound pollution problems. Further development of the process has apparently not been undertaken.

Economic and Technical Considerations - This process is chemically and mechanically complex. The major problems which plagued the demonstration plant were in the regeneration section in handling slurries and in difficulties in selling the ammonium sulfate. In addition, the manganese compounds which escape to the atmosphere from the scrubber are detrimental to public health and their elimination is a serious technical problem.

Applicability - The process has been tested on an oil-fired power plant. It produces ammonium sulfate which may be marketed. It can be retrofitted to a utility or industrial boiler but land requirements are high due to the large number of separate pieces of equipment required.

Summary and Conclusions - Development of the Mitsubishi Manganese Oxide process has ceased. Major determining factors in the cessation of development were the public health problems associated with the process, the overall energy requirements and complexity of the process, and the requirement that a nearby market for ammonium sulfate be found. Although the process received an intermediate rating, it should not be further investigated due to the extreme potential for producing harmful manganese emissions.

References - CA-327, SL-070

MITSUI ENGINEERING AND SHIPBUILDING PROCESS

Process/Subsystem Description - The Mitsui process is in the very early stages of development and little information is available. The flue gas is first passed through a prescrubber for chloride removal and gas cooling. It is then routed to the absorber where a ferrous chelate solution simultaneously absorbs sulfur dioxide and nitrogen oxides from flue gas. Sulfur dioxide is produced as a concentrated gas stream, while NO_2 is reduced to molecular nitrogen. The flue gas is then heated and exhausted through the stack.

Environmental and Energy Considerations - Bench scale testing on oil-generated flue gas demonstrated 95% removal of SO_2 and 85% removal of NO_x. Particulates and chlorides are removed in the prescrubber. Very little additional information concerning environmental and energy considerations is available.

Development Status - This process is in the early stages of development. It has been tested at the bench scale level on oil-generated flue gas. It has not been tested on coal-fired flue gas and it has not been integrated.

Economic and Technological Considerations - It is expected that this process will be fairly complex compared to other SO_2 removal processes.

Applicability - Very little is known about the applicability of this process to industrial or utility systems. The SO_2 produced may be a potentially marketable by-product.

Summary and Conclusions - This process design is in the very early stages and does not seem to offer advantages over other more advanced processes. Further consideration is not recommended.

References - FA-149

MOLTEN CARBONATE PROCESS

Process/Subsystem Description - The Atomics International Molten Carbonate process removes SO_2 from the flue gas at approximately 800°F and returns the still hot gases to the economizer and air preheater sections. Boiler gas at 800°F is routed through an electrostatic precipitator for ash removal and then countercurrently contacted with a eutectic mixture of molten Li_2CO_3, Na_2CO_3, and K_2CO_3 at 950°F to remove SO_2. The resulting SO_2-rich liquor is filtered to remove any residual ash and then regenerated with petroleum coke and air at 1400°F. The resulting stream containing sulfides of Na, Li, and K is then regenerated with CO_2 and H_2O to generate H_2S and carbonates of Na, Li, and K. The hydrogen sulfide stream is suitable for feed to a Claus plant and the regenerated metal carbonate is returned to the scrubber.

Environmental and Energy Considerations - The process is capable of achieving 90-95% SO_2 removal. Particulates are also removed. Fly ash filter cake which may contain lithium, sodium, and potassium will be discharged from the process. The L/G in the scrubber is low and no stack gas reheat is required. Petroleum coke is used as a reducing agent. In addition, energy is required to heat process equipment and piping. Raw materials required include makeup carbonate and petroleum coke.

Development Status - The molten carbonate process was tested with a 20,000 scfm (~10 Mw) pilot unit which was shutdown principally due to a series of corrosion problems. The reducer/regenerator was never operated. Because of the corrosive characteristics of the molten carbonate solution, the process does not appear to be viable and development has now ceased. Extensive use of novel technology would be required for process operation. Serious scale-up problems are anticipated.

Economic and Technological Considerations - The process is both chemically and mechanically complex. High temperatures must be maintained throughout the process equipment and piping to keep the molten carbonate mixture above its freezing point. Corrosion problems are serious.

Applicability - H_2S from the regenerator is sent to a condenser/cooler to reduce the water content of the gas and then to a Claus unit where it is converted to an elemental sulfur by-product.

Retrofit problems may be encountered because of the high temperature required for the flue gas stream sent to the absorber. Turndown, modularization, and decoupling of the process would be difficult.

Summary and Conclusions - This process had the lowest score in the wet regenerable process group. Because of its chemical complexity and severe corrosion problems, this process was not recommended for further evaluation.

References - BO-070, OP-004, SL-070

MOLTEN POTASSIUM CARBONATE/THIOCYANATE

Process/Subsystem Description - Garrett Research and Development Co. announced a process in which a slurry of K_2CO_3 in molten potassium thiocyanate (at about 350°F) is used to absorb SO_2. The resulting K_2SO_3, which is insoluble in the system, is separated and roasted with coal to form K_2S. The K_2S is reacted with CO_2 and H_2O to form H_2S. The K_2S is said to be converted to $KHCO_3$, which is separated by crystallization and calcined to give K_2CO_3 for recycle.

Environmental and Energy Considerations - Information on SO_2 removal was not found. Fly ash would be removed along with the SO_2. Energy requirements could be fairly high. No gas reheat or reducing gas is required, but coal is used to roast the K_2SO_3. Energy is also required to calcine the $KHCO_3$. The reduction and calcination steps are operated at high temperature. Some KSCN and K_2CO_3 makeup would be required as raw materials.

Development Status - The process has been tested only in the laboratory, and is no longer being developed. It apparently was not fully integrated. Use of new technology would probably be required, and serious scale-up problems could be encountered.

Economic and Technological Considerations - The process is quite complex, chemically and mechanically. The involved reactions proposed for sorbent recovery may not proceed without troublesome side reactions. Loss of absorbent must be prevented because of the high cost of the raw materials.

Applicability - By-product disposal should not limit applicability, since sulfur could be produced as a by-product. The absorption and regeneration operations could probably be decoupled. The process should be suitable for retrofit applications.

Summary and Conclusions - Not enough information was available to evaluate this process. It is capable of producing H_2S (which can then be converted directly to sulfur) without the need for a reducing gas. It is extremely complex, however, uses expensive absorbent raw materials, and has high energy requirements because of the high temperature reduction and calcination steps. The process is not recommended for further evaluation.

References - MC-308, SL-070

MORETANA CALCIUM

Process/Subsystem Description - In the Moretana process flue gas is passed through a prescrubber for particulate removal before it is oxidized with chlorine dioxide and passed through the absorber. The resulting nitrogen dioxide is absorbed along with the sulfur dioxide in the flue gas using a lime or limestone slurry containing a catalyst which aids in the absorption of the NO_x. After reheat, the gas is exhausted through the stack. By-product gypsum is produced and nitrates are to be removed from a purge stream by drying or reaction with ammonium carbonate.

Environmental and Energy Considerations - Bench-scale testing demonstrated SO_2 removal of 95% and NO_x removal of 90%. Particulates are also removed in the prescrubber. Environmental problems may be encountered in disposal of by-product gypsum, and chlorine dioxide presents a significant work hazard. Energy requirements include reheat for plume buoyancy, but reducing gas is not required. L/G ratios in the absorber are 20-45 gal/Macf. Raw materials required are limestone, sulfuric acid, catalyst, and the chemicals required to generate chlorine dioxide.

Development Status - This process has not been tested on flue gas from a coal-fired boiler. It has been tested in a prototype unit treating 15,000 scfm of flue gas from a sintering furnace. Also, it has been tested in a bench-scale unit using synthetic coal-fired flue gas. The calcium based process is a modification of the sodium-based process which has been tested more extensively. The process is integrated with the exception of the calcium chloride and calcium nitrate disposal portion. A decision concerning the method of disposal has not been made. Commercially available technology is used throughout most of the process. Scale-up problems may exist because of the lack of testing on coal-fired gas and the lack of development of the nitrate and chloride removal method.

Economic and Technological Considerations - Although the Moretana Calcium process is less complex than some of the other SO_x/NO_x processes, it is more complex than the conventional FGD systems. The chlorine dioxide generators add complexity and expense to the process. Process control becomes difficult because the chlorine dioxide generation requires significant time to adjust to changing levels of NO_x in the flue gas. Moretana plate towers are used in the prescrubber and absorber. Most of the equipment will be polymer-lined carbon steel, but some of the equipment will be made of Inconel 625 or 316L stainless steel.

Applicability - This process seems applicable in both industrial and utility situations. Decoupling should be relatively easy through intermediate storage. Retrofit is judged easy if enough land is available. Load following capabilities should be good. The gypsum by-product will probably have to be landfilled, as it cannot compete in the existing market. If a liquid fertilizer by-product is produced from the chlorides and nitrates, marketing might be possible.

Summary and Conclusions - The Moretana Calcium Process was rated below average. It has the capability to remove SO_2 and NO_x simultaneously, but complex processing steps are necessary. It has not been demonstrated on coal-fired flue gas. Further, it requires reheat and an expensive oxidant (chlorine dioxide). This process is not recommended for further consideration.

References - (TVA) FA-149

MORETANA SODIUM

Process/Subsystem Description - The Moretana Sodium Process employs ClO_2 to oxidize nitric oxide in flue gas. The resulting nitrogen dioxide is absorbed along with sulfur dioxide using a sodium hydroxide-sulfite solution. A prescrubber is used to remove particulates and chlorides before the gas is treated with ClO_2, passed through the absorber, reheated, and exhausted through the stack. Sulfate salts are recovered in solid form from the regeneration section.

Environmental and Energy Considerations - Prototype units operating on heavy oil-fired boilers have demonstrated 95% sulfur dioxide removal and 90% nitrogen dioxide removal. Particulates and chlorides are also removed. Disposal of the sodium salts presents a potential environmental problem due to their leachability. Energy requirements include the requirement for flue gas reheat. Reducing gas is not required, but chlorine dioxide is required, and it is fairly expensive to produce. The L/G ratio used in the absorber is 10-25 gal/Macf; the pressure drop is 200 mm of water. The major raw materials required are sodium hydroxide, sulfuric acid, sodium chlorate, and sodium sulfite.

Development Status - Five integrated prototype units (10-40 Mw) are in operation treating flue gas from heavy oil-fired boilers. This process has not been tested on coal-fired flue gas; it has been tested on gas from sintering furnaces and refuse incinerators. Commercially available technology is used throughout the process. Scale-up problems should be minimal because of operating experience with the process.

Economic and Technological Considerations - The Moretana Sodium Process, while less complicated than some of the other NO_x/SO_x processes, is more complex than conventional FGD systems. The chlorine dioxide generators add complexity and expense to the process. Process control becomes difficult because the chlorine dioxide generation requires significant time to adjust to changing levels of NO_x in the flue gas. Most of the equipment will be polymer-lined carbon steel, but some of the equipment will be made of Inconel 625 or 316L stainless steel.

Applicability - Moretana's Sodium Process is recommended only for small installations burning liquid or gaseous fuel. Their calcium based process is more suited to large coal-burning power plants. The major reason is the cost involved in the sodium-based process when applied to high sulfur flue gases. Retrofit should be relatively easy if sufficient land is available. Decoupling is readily achieved through intermediate storage; the medium L/G indicates less of a decoupling problem than in some of the other NO_x/SO_x processes. Load following is difficult because of the unsuitability of the ClO_2 production section in such applications. By-products may have a limited market depending upon regional situations.

Summary and Conclusions - This process rated higher than the other NO_x/SO_x processes, mainly because of its development status but relatively low compared to processes for SO_2 removal alone. It is more complex than conventional FGD systems; it requires an expensive gas (chlorine dioxide); it requires flue gas reheat; and it has not been tested on coal-fired boilers. This process is not recommended for further consideration.

NIIOGAZ AMMONIA/STEAM STRIPPING PROCESS

Process/Subsystem Description - This process, developed by NIIOGAZ in the USSR, utilizes ammonia scrubbing followed by thermal stripping. Flue gas is cooled with cooling water in the first section of the scrubber where about 10% of the SO_2 is absorbed. The gas is then scrubbed with ammonia in three stages. The final stage in the scrubber is an electrostatic precipitator used as a mist eliminator. The scrubbing solution is regenerated by thermal stripping carried out by indirect heating with steam. A stream of SO_2 is evolved. A side stream of scrubbing solution is autoclaved to remove the ammonium sulfate formed by sulfite oxidation and the thiosulfate and polythionate formed by solution decomposition in the generator producing ammonium sulfate and sulfur by-product.

Environmental and Energy Considerations - SO_2 removal of 90% is possible. Chlorides may be removed in a pre-wash section, but there does not appear to be potential for removing other pollutants. Secondary pollution can result from ammonia plume formation and from disposal of the gas cooling water. The water is neutralized with lime before disposal. Energy requirements are high because of the large amount of steam required for thermal stripping. Scrubber pressure drop is low, but gas reheat will be required. Raw materials required (excluding those needed to process the product stream of SO_2) include ammonia, lime for neutralizing the cooling water, and possibly an inhibitor to reduce oxidation.

Development Status - The process was operated on a 65-MW boiler from 1952 to 1961 in Russia, and a full scale demonstration is planned for a 300 MW coal-fired boiler. The process has not been fully integrated. It uses current technology and only minor scale-up problems would be anticipated.

Economic and Technological Considerations - The ammonia scrubbing process is chemically and mechanically complex because of the problem of plume formation. The chemistry of the regeneration section is somewhat simpler. High steam consumption in the thermal stripper is a major problem.

Applicability - Concentrated SO_2 is produced as a by-product from this process, along with small amounts of ammonium sulfate and sulfur. Retrofits should not be difficult, but decoupling and modularization would probably be difficult due to low absorbent loading.

Summary and Conclusions - The NIIOGAZ Ammonia Scrubbing process rated high among the wet regenerable FGD processes. The primary reason for its rating was its advanced status of development. Other major advantages of the process include minor solid waste disposal problems and low scrubber pressure drops. Disadvantages of the process include large energy requirements for regeneration, secondary pollution from ammonia plume formation, and the high cost and questionable feasibility of nonadiabatic flue gas cooling. Although this process is not recommended for individual evaluation, it should be evaluated as a part of the absorption and steam stripping evaluation.

References - CA-327, SL-070

NIIOGAAZ MAGNESIUM OXIDE

Process/Subsystem Description - Flue gas is cocurrently contacted with a magnesium oxide slurry which reacts with SO_2 to form magnesium sulfite with simultaneous magnesium sulfate formation from SO_3 absorption. The magnesium sulfate is removed from the scrubber slurry by hydrocloning and vacuum filtration of a slip stream. The magnesium sulfite is dried and calcined to form magnesium oxide and SO_2 with the SO_2 going to an acid plant. Another scrubber slurry slip stream is filtered for ash removal. Fresh magnesium oxide makeup, recycled magnesium oxide from the calciner, filtered solutions from the ash filter and the vacuum filter and scrubber slurry are mixed in a tank and recycled back to the scrubber.

Environmental and Energy Considerations - The SO_2 removal efficiency is reported to be 92% to 95%. Removal of other pollutants was not reported. An L/G of around 20 gal/1000 scf was reported, and stack gas reheat will be required. Energy is also required to dry and calcine the magnesium sulfite. No reducing gas is needed. Pressure drop through the system is not expected to be large. Magnesium oxide makeup is required as a raw material.

Development Status - Tests have been conducted at pilot level at a sintering plant and a power plant. Installation of a 300 MW system at a power station is reportedly being considered. The process has not been fully integrated. Some minor scale-up problems may occur. Current technology is used in the process.

Economic and Technical Considerations - The process is mechanically and chemically complex and requires energy for drying and calcining magnesium sulfite It is reported that oxidation was not a problem and scaling was minimal.

Applicability - This process is applicable for coal-fired plants but requires an acid or sulfur plant for the disposition of the by-product SO_2. The process can be turned down, retrofitted, and modularized. Process sections can be decoupled.

Summary and Conclusions - The NIIOGAAZ process rated as the highest scorer in the preliminary evaluation of the FGD wet regenerable class. The most notable advantages of the NIIOGAZ process are apparent when comparing it to the Wellman-Lord process. These advantages include a simpler scrubber design and no reported problems with oxidation. Certain disadvantages are associated with this process, however. These include an SO_2 by-product stream which is relatively dilute (15%) and the need for fuel oil in the regeneration step. This process is recommended for further evaluation and will be discussed in the Mag-Ox technical summary paper.

References - CA-327

NOSOX PROCESS

Process/Subsystem Description - In this process, SO_2 is absorbed in a clear solution of ethanolamine glutarate. The solution is regenerated by steam stripping to produce concentrated SO_2. Sulfate would probably be removed as gypsum by lime neutralization of a purge stream.

Environmental and Energy Considerations - The NOSOX process has potential for SO_2 removal efficiencies greater than 90 percent, but has no multipollutant removal potential. Secondary pollutant problems include the sulfates which would need to be disposed of. Also, the escape of any absorbent to the environment would be dangerous. Some reheat of the flue gas would be required. No reducing gas is needed for regeneration. The steam required for stripping SO_2 from the absorbent is potentially less than that needed for Wellman-Lord. The L/G and pressure drop should not be high. Raw materials include ethanolamine, glutaric acid, and possibly lime for sulfate removal.

Development Status - The system has been tested at the bench-scale level. It has not been integrated. Current technology is used in all steps, except SO_2 conversion, and therefore only minor problems should be associated with scale-up.

Economic and Technological Considerations - The chemistry of the NOSOX process is well understood and relatively simple. Ethanolamine may catalyze sulfite disproportionation to sulfate, however. Mechanically the process is simple and well understood.

Applicability - No serious problems appear to limit the NOSOX process at this stage from utility and industrial application. Turndown and retrofit should be possible, as well as industrial modularization of the equipment. However, decoupling the absorption and regeneration steps may be difficult due to expense of the absorbent solution. By-product marketability should be good.

Summary and Conclusions - The NOSOX process rated average among the wet regenerable processes. This was primarily because of low scores due to its limited development and decoupling inability combined with a high score for its overall process simplicity. Advantages include potentially lower steam requirements and easier sulfate solid waste handling relative to Wellman-Lord. Disadvantages include the high cost of absorbent makeup, potential secondary pollutant problems from absorbent loss, and the possibility of ethanolamine catalizing sulfite disproportionation to sulfate. Although the process is not recommended for an individual evaluation, it should be evaluated as part of the general evaluation of absorption and steam stripping.

References - MC-305

PEABODY PROCESS (CITRATE/STEAM STRIPPING)

Process/Subsystem Description - In this process, SO_2 is absorbed in a solution of sodium citrate which is regenerated by steam stripping to give concentrated SO_2. Sulfate is removed by refrigerated crystallization of Glauber's salt. This version of the Citrate process suggests stripping at elevated pressure and temperature so that liquid SO_2 can be directly produced.

Environmental and Energy Considerations - The Citrate Steam Stripping Process is capable of good SO_2 removal efficiencies, reportedly up to 99 percent. No multipollutant removal potential exists or is suspected. Sodium sulfate is the only secondary pollutant resulting from the process. Stack gas reheat is required, but no reducing gas is needed for regeneration. Other energy requirements include steam for stripping the citrate solution for SO_2 removal. Pressure drop through the absorber is not large. Material requirements include sodium citrate makeup.

Development Status - The stripping process has been tested at the bench-scale level by U.S. Bureau of Mines and Peabody. Integration with the absorption step has not been attempted. The process uses current technology in all areas and for this reason few scale-up problems are suspected.

Economic and Technological Considerations - The chemistry of the absorption step is very simple. The stripping step is also chemically simple as long as the temperature is kept below 212°F to prevent sulfite disproportionation. Likewise, mechanically the process is relatively simple. Prescrubbing before the absorber is necessary, however, to exclude chlorides from the stripper.

Applicability - No serious problems are apparent with this process which might limit its applicability to utility or industrial applications. The process has good turndown capability, can be retrofitted, and can be modularized for industrial application. Decoupling of the process steps may be difficult, however.

Summary and Conclusions - The Citrate Steam Stripping Process rated relatively high among the wet regenerable FGD processes. The good rating was primarily due to the overall chemical and mechanical simplicity of the process. Advantages of the process include good SO_2 removal potential, minor solid waste disposal problems, and the overall process simplicity. Disadvantages include potentially larger steam requirements than the Wellman-Lord process and costly citrate makeup unless losses are carefully controlled. This process concept should be examined further as part of the absorption/steam stripping evaluation.

References - ST-511

POTASSIUM FORMATE PROCESS

Process/Subsystem Description - SO_2 is absorbed by a concentrated potassium formate solution, producing thiosulfate. The thiosulfate is reacted with additional formate to produce hydrosulfide which is stripped with CO_2 and steam to release H_2S and form potassium carbonate and bicarbonate. Potassium formate is regenerated by reducing the carbonate and bicarbonate with CO at high pressure. The H_2S is converted to sulfur in a Claus plant. The Potassium Formate process was developed by the Research Division of Consolidation Company in the late 1960's and early 1970's, but has been abandoned in favor of the Consol Process.

Environmental and Energy Considerations - The process is capable of 90% SO_2 removal, but does not appear to have potential for multipollutant removal. Secondary pollution from H_2S could be a problem under some circumstances. L/G and pressure drop appear to be low, but a reducing gas will be required for regeneration. Gas reheat will be necessary. Raw materials required are a source of potassium makeup and a reducing gas.

Development Status - The process was tested at the bench scale, but further development led to the Consol process, which uses an absorbent solution of KHS, $KHCO_3$, and K_2CO_3, with K_2S_x and KOOCH as minor components. The process apparently was only partially integrated. Extensive use of novel technology appears to be required. Serious scale-up problems are anticipated.

Economic and Technological Considerations - This process is extremely complex, chemically and mechanically. Sorbent regeneration requires a complex series of operations which would be difficult to control in a full-scale plant.

Applicability - This process appears to be generally applicable for utility or industrial use. It can be turned down, retrofitted, and modularized. Process sections can be decoupled. Sulfur is produced as a by-product.

Summary and Conclusions - This process scored very low compared to other wet regenerable processes. It scored well in applicability, but it is quite complex and is not well developed. It also scored low in environmental and energy consideration because of its high energy requirements. The major disadvantages of this process are high energy requirements, need for a reducing gas, and extreme chemical and mechanical complexity. It is not recommended for further evaluation.

References - MC-303, ST-504, YA-001

POTASSIUM SULFITE PROCESS

Process/Subsystem Description - In this process, developed by Wellman Lord, flue gas is scrubbed with an aqueous solution of K_2SO_3. The SO_2 reacts with the K_2SO_3 to form $K_2S_2O_5$ which is then thermally stripped to regenerate K_2SO_3 and release SO_2. The SO_2 can be used to produce sulfur or sulfuric acid.

Environmental and Energy Considerations - SO_2 removal efficiency of more than 90% is possible. There does not appear to be potential for multipollutant removal. Energy requirements for the process are relatively high; a large amount of heat is required for the regeneration step and the flue gas must be reheated. The L/G and pressure drop for the scrubber are not high, however. Raw materials required include a source of potassium makeup. A potassium sulfate stream must be disposed of or sold.

Development Status - The process was tested at a 50,000 scfm (∿28 MW) prototype unit at Baltimore Gas and Electric's Crane Station in 1969. This unit was shut down after 9 months because of the very high energy requirements for the thermal stripping and because of difficulties from fly ash plugging the absorber. Development efforts were then shifted to the sodium system for absorption, the present day Wellman-Lord process. Scale-up problems for the potassium sulfite process could be severe.

Economic and Technological Considerations - Scaling problems may be experienced in potassium absorption systems because of the relative solubilities of potassium sulfite and bisulfite (or pyrosulfite, the anhydride of bisulfite). In potassium systems the bisulfite (or pyrosulfite) is much less soluble than sulfite. Thus, as SO_2 is absorbed, less soluble compounds are formed and water is evaporated in the scrubber. Pyrosulfite scaling can occur. Thermal stripping of pyrosulfite requires a large amount of energy. Development of sulfite during stripping rapidly decreases the SO_2 vapor pressure, making the H_2O/SO_2 vapor pressure ratio (which controls the amount of heat required) high. The chemistry of the process is complex in all areas. However, mechanically the scrubbing and regeneration areas are simple.

Applicability - A stream of concentrated SO_2, suitable for sulfuric acid or sulfur production, is produced as a by-product.

The absorption and regeneration steps could be decoupled relatively easily, and retrofits should not be difficult. The system should be suitable for industry modularization and utility and industry turndown ability should be good.

Summary and Conclusions - The Potassium Sulfite process rated average among the wet regenerable processes. This rating is due primarily to the process' chemical complexity, severe scale-up problems, relatively undeveloped state, and high energy requirements. The process is not recommended for further consideration.

References - CA-327, CR-005, SL-070, WE-015

PRODUCTION OF REDUCING GAS

Process/Subsystem Description - Many FGD systems and subsystems require the use of H_2/CO reducing gas for the reduction of SO_2 to H_2S and sulfur. Industrially, reducing gases are presently produced by the incomplete combustion of natural gas and fuel oils. However, because of the decreasing availability of natural gas and fuel oils, the gasification of coal is considered as the most likely source of reducing gas for FGD systems.

In the gasification reaction, coal is reacted with steam and/or oxygen to produce a gas rich in H_2/CO. Particulates, unreacted hydrocarbons and other impurities can be cleaned from the coal gasifier gas. Some of the FGD systems require very clean reducing gas streams in order to produce a saleable by-product.

Environmental and Energy Considerations - For many of the coal gasification processes, clean up of the reduction gas produces serious waste water treatment problems. In addition, coal gasifiers can introduce serious air and solid waste environmental problems. Based on coal feed energy content, coal gasifiers are about 65 to 75% energy efficient.

Development Status - There are a number of coal gasification processes which have been in commercial operation since the 1950's. In addition a number of coal gasification processes are presently at various stages of development in the U.S.

Economic and Technological Considerations - Presently, the capital and operating costs for coal gasification are high. Although a number of commercial coal gasification plants are in operation, the gasification reaction is complex, and many mechanical problems exist. In addition a number of environmental problems remain to be identified and solved.

Applicability - Depending on the selection of the gasification process, almost any coal or lignite burned at a power plant could be gasified to produce an acceptable reducing gas.

Summary and Conclusions - Although the use of natural gas and fuel oil to produce reducing gas requires much lower capital and operating costs, the decreasing availability of these fossil fuels make coal the likely raw material source for FGD systems at coal-fired facilities. The systems for producing reducing gas are either commercial or being funded at a high level at this time. However, the integration of a coal gasification system with an FGD system has not been achieved and it is recommended for consideration as a process alternative in the next stage of this study.

PURASIV S

Process/Subsystem Description - The Purasiv S process is a molecular sieve system designed to remove SO_2 from the vent gas of a sulfuric acid plant. The vent gas, having a maximum of 3500 ppm of SO_2, passes through a fixed molecular sieve bed which removes 98-99% of the SO_2. The molecular sieve bed is thermally regenerated with air in a batch mode to produce a 4% SO_2 stream. This stream is then used for combustion in sulfuric acid plants.

Environmental and Energy Considerations - This process has a high SO_2 removal efficiency. Maximum sieve bed temperature is 170°F, consequently, a flue gas may have to be cooled before treatment and reheated for discharge to the stack. Removal of other pollutants has not been demonstrated. Regeneration of the molecular sieve bed will require energy to heat the regeneration air. A dilute SO_2 stream is produced upon regeneration which is used for combustion in a sulfuric acid plant.

Development Status - This process has been used commercially since 1973.

Economic and Technological Considerations - Capital costs were reported between $30/1000 scfm to $60/1000 scfm (October 1973) with operating costs between $0.1/1000 scfm and $0.2/1000 scfm (1973).

Applicability - This process was developed for sulfuric acid plant tail gas SO_2 removal. The process can only handle 100 ppm of H_2O, thus it would not be applicable for SO_2 removal from flue gas.

Summary and Conclusions - This process is a commercially available process applicable to removing SO_2 from sulfuric acid plant tail gases. However, it is not applicable to flue gas desulfurization in boiler applications because of its lack of tolerance for water in the stream being treated. It is not recommended for further consideration.

References - CO-142

RALPH M. PARSONS PROCESS

Process/Subsystem Description - Operation in the boiler is modified so that a neutral or slightly oxidizing atmosphere is maintailed in the boiler. This is done by minimizing the excess air to the boiler and injecting a hydrocarbon fuel, such as natural gas or producer gas, into the radiant zone of the boiler. The flue gas passes through a hot ESP to remove particulates before being sent to a catalytic reduction reactor. The SO_2 is converted to H_2S and the NO_x is converted to N_2. The flue gas then goes through the boiler air heater and through a Stretford absorber to remove the H_2S. The H_2S is further reduced to elemental sulfur in the Stretford unit.

Environmental and Energy Considerations - Since the conceptual process has never been tested, the NO_x and SO_2 removal efficiencies which can be achieved are unknown. High removal efficiencies for both SO_2 and NO_x require that a reducing atmosphere be generated before entering the catalytic reactor to chemically remove any free oxygen. This reducing atmosphere will result in the formation of several toxic gases including carbon monoxide, hydrogen sulfide, and carbonyl sulfide. Most of these gases will be converted to harmless compounds in the reactor or absorbed in the Stretford abosrber. But, complete conversion or absorption is not possible so that the residuals exiting in the flue gas are a potentially serious pollution problem. The process will require some hydrocarbon fuel such as natural gas.

Development Status - The process is in the conceptual design stage and has not been tested in a bench-scale unit. However, this process utilizes, in part, technology previously developed jointly by the Union Oil Company and Ralph M. Parsons Company during commercialization of the Beavon Sulfur Removal process.

Economic and Technological Considerations - The reduction reactor is chemically simple but the Stretford unit is complex chemically. The overall process is mechanically simple. The large volume of flue gas that must be treated in the Stretford unit would require a large unit that could seriously impact process economics.

Applicability - The process can be decoupled between the Stretford absorber and the Stretford oxidizer by using storage tanks. The process should also follow load changes very rapidly. The process is not well suited for retrofitting because the hot ESP and reduction reactor must be placed between the economizer and air heater. However, it could be retrofit through reheat of the flue gas to reactor temperature.

Summary and Conclusions - The Ralph M. Parsons process is at the conceptual stage of development. The process has a serious potential secondary pollution problem with residual H_2S, COS, and CS_2 exiting with the flue gas. This process should not be considered further.

References: FA-149

RED MUD

Process/Subsystem Description - Red Mud is the commonly used name for the material remaining after alumina has been extracted from bauxite ore in the Bayer process. In bench scale testing done by the U.S. Bureau of Mines, Red Mud was used to sorb SO_2 from a simulated flue gas in several different types of reactor beds. Thermal regeneration of the red mud was attempted and found to be only partially successful. The red mud was found to exhibit approximately half of the SO_2 removal efficiency of limestone.

Environmental and Energy Considerations - Relatively low SO_2 removal efficiencies would probably be achieved with Red Mud. No other pollutants appear to be removed from the flue gas, but the Red Mud used as sorbent is a waste product from aluminum manufacturing that is currently being landfilled or ponded. Disposal of the waste material (containing metal sulfites, sulfates and fly ash) after SO_2 absorption could cause serious secondary pollution problems. Stack gas reheat will be required and L/G and pressure drop will be relatively high. Energy requirements for the regeneration of Red Mud would be very high.

Development Status - The Bureau of Mines discontinued development in 1969. Pilot testing has been conducted by Knipp Research Center in Essen, West Germany. Mitsubishi Heavy Industries in Tokyo has also done pilot work using a slurry of red mud. However, in view of the current status of research and development effort, there is little possibility of commercialization of this process in the foreseeable future. Commercial technology is used in the process, but apparently the process has not been fully integrated. Serious scale-up problems would be expected.

Economic and Technological Considerations - This process appears to be quite complex both chemically and mechanically. The only raw material costs associated with the use of red mud would be the transportation costs and the cost of slurrying, extruding or pulverizing the red mud. Raw material consumption, energy requirements and capital costs would be difficult to estimate with the limited amount of experimental data. They are, however, expected to be greater than for limestone scrubbing since the Red Mud solvent is only half as reactive as limestone.

Applicability - Applicability is limited to power plants in locations where Red Mud is available and where the waste product may be disposed. The process can be turned down and decoupled, but retrofits and modularization would be difficult.

Summary and Conclusions - This process scored well below average compared to other throwaway processes in all four categories. It has the advantage of using a solid waste as the sorbent, but a high temperature reactor would probably be required.. Achieving adequate SO_2 removal would be difficult. In addition, applicability is limited to areas where Red Mud is available. This process is not recommended for further evaluation.

Reference - HA-643

REDUCTION WITH BLUE GAS

The process for removing sulfur and nitrogen oxides from stack gases by reduction with "blue gas like compositions" was conceived by Dr. E. J. Schwoegler of Schwoegler Labs. The process is only at the conceptual stage. Dr. Schwoegler claims to have sufficient data to show favorable economics for his process but was unwilling to release more information for fear that someone else would develop the idea. The project is currently on hold; he wants to do more work on it but will not do so unless he can be assured of funding.

Reference - SC-452

RESOX

Process/Subsystem Description - RESOX is a proprietary process for the production of elemental sulfur from an SO_2-rich gaseous stream as produced by various regenerable SO_2 removal processes. Crushed anthracite coal moves downward while the SO_2-rich stream moves upward in the countercurrent reactor. About 90 percent of the inlet SO_2 is reduced to vapor phase elemental sulfur. The RESOX product gas then passes to an inclined shell-and-tube condenser where boiler feedwater is converted to 50 psig steam on the shell side and gaseous elemental sulfur condenses on the tube side. The molten sulfur is collected and either stored at elevated temperatures as a liquid or sent to pits to solidify.

Environmental and Energy Considerations - The condenser off-gas could contain unreacted SO_2, H_2S, COS, and CS_2 and therefore is not suitable for venting. This stream would be routed to an incinerator or to the boiler. The ash and unreacted or unburned coal leaving the bottom of the reactor must be fed to the boiler or combined with other ashes for disposal.

Development Status - The RESOX process has been demonstrated at the 47.5 MW level in an integrated system employing the Bergbau-Forschung/Foster Wheeler Dry Adsorption Process.

Economic and Technological Considerations - The cost of RESOX coal is a primary consideration in the cost analysis of an integrated system. The coal used in the RESOX unit must have a low volatile content. Anthracite coal is currently specified for RESOX. Decreasing production and high shipping costs from Pennsylvania may be significant problems until other coals are evaluated.

Applicability - RESOX units can be located remote from the stack, so the process is applicable to retrofit installations. The proposed sizing in 150 MW modules is also well suited to boiler turndown ability, especially for larger boilers where numerous modules would be required.

Summary and Conclusions - This subsystem directly reduces SO_2 to sulfur by contact with anthracite coal and has been demonstrated in a fully integrated FGD system. Off gas from the subsystem requires treatment for removal of sulfur compounds and the cost and availability of anthracite coal are of concern. However, because this subsystem directly converts SO_2 to sulfur without requiring the generation of a reducing gas, the process has been recommended for further evaluation.

References - OT-R-051

RIIC PROCESS

Process/Subsystem Description - In the RIIC process, flue gas is scrubbed with ammonia in two scrubbers in series. Effluent scrubber solution is acidulated with nitric acid in a decomposition/distillation column, forming ammonium nitrate and evolving SO_2. The ammonium nitrate is used for fertilizer production. The SO_2 produced may be contaminated with NO_x, which would damage the catalyst in a contact type sulfuric acid plant.

Environmental and Energy Considerations - SO_2 removal efficiency greater than 90 percent is possible. No other pollutants are removed. As with other ammonia scrubbing processes, plume formation may be a serious problem. No reducing gas is required, but stack gas reheat is. Steam is also required for the decomposition/distillation column. Ammonia and nitric acid are required as raw materials.

Development Status - The process, developed by RIIC, has been applied commercially to clean tail gas from a 300 tpd sulfuric acid plant in Czechoslavakia. The process has been integrated. In general, it uses commercial technology. Some scale-up problems may be encountered in applying the process to power plant flue gas.

Economic and Technological Considerations - The process is relatively complex, chemically and mechanically. Scrubber design is complicated by the volatility of ammonia and the possibility of plume formation. Careful operation of the decomposition column is necessary to minimize NO_x evolution and prevent contamination of the SO_2 stream with NO_x. The NO_x can damage the catalyst if the SO_2 is used to produce sulfuric acid. Oxidation in the system can result in contamination of the ammonium nitrate with sulfate.

Applicability - Applicability of the process is limited to areas where a market for ammonium nitrate exists. Concentrated SO_2 which may be difficult to convert to sulfuric acid is also produced as a by-product. The process can be turned down and retrofitted, and could be modularized and decoupled with additional equipment.

Summary - The ammonium nitrate produced as a by-product is a more popular fertilizer and has better sales potential than the ammonium sulfate produced in many other ammonia processes. The SO_2 stream, possibly contaminated with NO_x, would be more dificult to process into H_2SO_4 than that from other processes. Ammonia plume formation can be a serious problem. The process did not score well compared to other throwaway processes and therefore is not recommended for further evaluation.

References - CA-327, SL-070

ROHM AND HAAS RESIN ADSORPTION PROCESS

Process/Subsystem Description - In the Rohn and Haas Process, SO_2 is adsorbed on a moving bed of ion exchange resin. The flue gas must be prescrubbed for particulate removal and cooling. SO_2 laden resin from the adsorber is transferred to a regeneration section where the SO_2 is steam stripped at a temperature of about 260°F to produce a concentrated SO_2 gas which is suitable for sulfur or sulfuric acid production.

Environmental and Energy Considerations - SO_2 removal efficiencies of 90-95 percent have been reported. The process does not appear to achieve multipollutant removal. Stack gas reheat may not be required and no reducing gas is needed. Steam requirements are potentially low (theoretical requirements are 2½ pounds steam/pounds SO_2), however, there are insufficient data to determine the actual steam requirements. Pressure drop will probably be greater than for wet absorption systems. Makeup resin requirements are anticipated to be low.

Development Status - Some bench scale data have been taken. Major gaps exist concerning engineering design data. The developer is currently performing internal evaluations of the process that will determine if future development activities are warranted. The process appears to use components that are commercial in other applications and should have minor scale-up problems.

Economic and Technological Considerations - The chemistry of the process appears relatively simple. Absorbed SO_2 is thought to form complexes which can be easily steam stripped, and thus, the steam requirements are thought to be low. However, data are not currently available to verify this. The solids handling equipment required to transport the resin between the absorber and the regenerator will increase the overall process mechanical complexity.

Applicability - There is no apparent problem that would limit the process applicability except, perhaps, the requirement for solids handling equipment between the absorption and regeneration sections. Turndown ability appears reasonable, however, retrofitability may be hindered by the solids handling equipment. Decoupling the absorption and regeneration sections could be accomplished by adding resin storage facilities. By-product marketability should be good.

Summary and Conclusions - The Rohm and Haas Resin Adsorption process rated well above average when compared to other dry systems. This rating is due primarily to its relative mechanical simplicity and its potential for low steam requirements. The process will be examined as a process alternative as part of the Sorption/Steam Stripping evaluation.

Reference - BO-289

SCRA PROCESS

Process/Subsystem Description - The SCRA (Smelter Control Research Associates) process is an ammonia-based double alkali process that uses limestone for regeneration. Gas is scrubbed with a solution of $(NH_4)_2SO_3$. SO_2 reacts to form NH_4HSO_3. Spent scrubbing liquor is reacted with limestone to regenerate the $(NH_4)_2SO_3$ and produce calcium sulfite solids for disposal.

Environmental and Energy Considerations - SO_2 removal of 95% or greater should be possible. The process does not appear to have potential for multipollutant removal. Secondary pollution problems could result from ammonia plume formation and sludge disposal. Energy requirements should be relatively low. Stack gas reheat is required, but no reducing gas is needed and L/G and pressure drop should be relatively low. Limestone and ammonia are required as raw materials.

Development Status - The process was developed for use on smelter waste gases containing high concentrations of SO_2. It has been tested at the pilot plant level. Commercial technology is used in most process areas. Scale-up problems may be experienced, especially in the absorption area.

Economic and Technological Considerations - The process appears to be somewhat complex, chemically and mechanically. Scrubber design is complicated by the volatility of ammonia and the possibility of plume formation. The process was developed for treating smelter gases with a high concentration of SO_2. Treatment or flue gas with a low SO_2 concentration may be more difficult.

Applicability - This process can reasonably be turned down, retrofitted, and modularized. Process sections can be decoupled through use of intermediate storage. Applicability could be limited by the need to dispose of large quantities of waste. Since the process has not been developed on low concentration SO_2 streams, applicability to flue gas desulfurization is unknown.

Summary - The SCRA process scored relatively low compared to other throwaway processes. It has the advantage of using limestone, rather than lime, for regeneration. As with other ammonia scrubbing processes, however, formation of an ammonia plume can be a serious problem. This process is not recommended for further evaluation.

References - SL-070.

SEA WATER SCRUBBING

Process/Subsystem Description - Sea water has been proposed as an absorbent for SO_2. A countercurrent gas-liquid contactor would be used to absorb SO_2 from the flue gas, and the weak sulfuric acid solution (~pH 6) could be returned directly to the sea. It would be a low capital process and problems with regeneration and disposal would be eliminated.

Environmental and Energy Considerations - SO_2 removal of 90% or more appears to be possible. The process does not appear to have potential for multipollutant removal. Discharge of the weak sulfuric acid solution which also contains nitrates and fly ash into the ocean could result in severe secondary pollution problems. Energy requirements would be relatively high. Reheat would be required, and L/G and pressure drop would be high. The only raw material required is sea water.

Development Status - This process remains at bench scale.

Applicability - Applicability of this process is limited to power plants on the coast, where sea water can be withdrawn and returned. The process can be turned down and modularized, but retrofits would be difficult because of the large absorber that would be necessary.

Summary and Conclusions - This process scored below average compared to other throwaway processes. It is relatively underdeveloped and scored below average in applicability and well below average in Environmental and Energy Considerations. Conceptually, this process is very simple. However, major environmental problems would be encountered with dumping low pH sea water containing ash and nitrates into the ocean. In addition, corrosion and scaling problems may be encountered. This process is not recommended for further evaluation.

References - BR-415

SHUFFMAN PROCESS

Process/Subsystem Description - The Shuffman Process utilizes a packed bed of ice which has been chilled by liquid nitrogen. The flue gas, which flows through the bed, is cooled sufficiently to freeze out water and SO_2 in the flue gas. The ice containing H_2SO_3 and H_2SO_4 is then utilized in the manufacture of sulfuric acid.

Environmental and Energy Considerations - Effective SO_2 removal should be possible. Removal of particulates, NO_x, and other gases is also claimed. Low energy consumption is claimed, but this does not take into account the extremely large energy requirements for the production of liquid nitrogen, for stack gas reheat, or for production of sulfuric acid. No reducing gas is required and the only raw material is air for production of liquid nitrogen.

Development Status - The process remains at the conceptual stage. Further development potential would appear to be extremely limited by energy and technical considerations.

Economic and Technological Considerations - The concept of the process is simple; however, a rather complex cooling system and solids handling system may be required to operate it. Operation of a packed bed of ice with additional ice created by freezing water out of the flue gas would be difficult.

Applicability - There appear to be no fuel constraints. Special materials of construction may be required in some areas because of the low temperatures and the production of dilute sulfuric acid. Retrofits may be difficult due to the large size of the ice beds. Turn down would be inhibited by the requirements of the fluidized beds.

Summary and Conclusions - The process does not appear to have any significant technological advantages over other processes presently available or under development. The high energy requirements are a major disadvantage. In addition to these technical problems, the process is at the conceptual stage and is not recommended for further consideration.

References - RO-320, SH-338

SIMON CARVES PROCESS

Process/Subsystem Description - In this process, flue gas is scrubbed with ammonia to produce ammonium sulfate. The ammonia can be supplemented with H_2S or manganous ions to promote better oxidation of ammonium sulfite to ammonium sulfate. A portion of the scrubbing solution is filtered to remove any fly ash and then treated in an autoclave to produce sulfur by reaction with H_2SO_4.

Environmental and Energy Considerations - High SO_2 removal efficiencies are indicated by test units. Formation of an ammonia plume can result in severe secondary pollution problems. Operational energy requirements appear to be average for wet scrubbers, however, the autoclave requires a significant energy input. L/G and pressure drop are relatively low. Stack gas reheat is required.

Development Status - A 56,000 cfm (30 Mw equivalent), integrated plant has been operated on a coal-fired boiler. TVA (U.S.), Simon-Carves (U.K.), Cominco (Canada), and Niiogaz (USSR) have studied this process. However, no commercial development has been attempted. Some use of noncommercial technology would probably be required and scale-up problems may be encountered.

Economic and Technological Considerations - This process appears to be rather complex both chemically and mechanically. Major process drawbacks include a potential explosion hazard and corrosion in the autoclave reactor.

Applicability - This process has no apparent liabilities that affect its suitability for retrofit or turndown. Decoupling can be accomplished through intermediate storage. The sulfur and ammonium sulfate by-products are potentially marketable.

Summary - The process scored below average compared to other wet processes. The overall process complexity and lack of continued development are the primary liabilities. This process is not recommended for further evaluation.

References - CA-327

SLUDGE STABILIZATION

Process/Subsystem Description - Several commercial processes are currently available to stabilize ash and sludge. Sludge stabilization is directed toward decreasing leachability of the sludge, increasing its load bearing ability and in general increasing its environmental acceptability as a landfill material. The Dravo Calcilox® Process consists of the addition of Calcilox® and lime to produce the waste product. The IU Conversion System's Poz-O-Tex® Process uses the addition of fly ash and lime to stabilize the sludge. Chemfix stabilizes the waste product with their Chemfix® Process which involves the addition of sodium silicate and Portland cement.

Environmental and Energy Considerations - The sludge fixation processes produce no secondary pollution problems apart from possible problems associated with the stabilized sludge. The processes have been shown to produce a stabilized waste product which has a much improved load-bearing ability. Leaching of pollutants from the sludge is also reduced but could still pose an environmental problem. The processes are very low in energy consumption. Raw materials required are generally settling agents such as lime, fly ash, or some proprietary additive.

Development Status - The Dravo Process has been operated since 1974 on a full-scale FGD system at the Bruce Mansfield Plant (1828 Mw) of Pennsylvania Power Company. One full-scale (403 Mw) IUCS system has been operating since 1976 at the Conesville Plant of Columbus and Southern Ohio Electric Company. Three additional plants, totaling 1415 Mw, are expected to be fully operational by November, 1977. Chemfix experience with FGD scrubber sludges is limited to EPA tests conducted at Shawnee and other tests at the Will County Plant. Chemfix does have demonstrated experience with hazardous industrial and municipal wastes.

Applicability - These processes could be used on any FGD system that produces a $CaSO_3/CaSO_4$ sludge. Generally, sludges with any sulfite/sulfate ratio and with or without fly ash can be used. Higher solids content of the sludge is preferential to reduce the additive requirement and to insure proper stabilization of the sludge.

Economic and Technological Considerations - The incremental costs of the systems above ponding of unstabilized sludge is fairly significant. The additive requirement is a major portion of the annualized cost. Energy requirements for the systems are low as energy is needed only for solids transport and slurry pumping.

Summary and Conclusions - Sludge fixation processes have demonstrated that they can improve the physical stability of $CaSO_3$/$CaSO_4$ sludge. The process developers also claim a reduction in the amount of contaminants leached out of the sludge. Leaching does still take place and is a potential problem with the processes.

Reference - AE-016

SODIUM CARBONATE WET THROWAWAY

Process/Subsystem Description - SO_2 is absorbed in a recirculating solution of Na_2SO_3 which is continuously neutralized by addition of Na_2CO_3. Japanese processes crystallize Na_2SO_3/Na_2SO_4 solids by adding solid Na_2CO_3. U.S. processes generally produce Na_2SO_3/Na_2SO_4 solution which is sent to evaporation ponds. Oxidation to Na_2SO_4 is optional.

Environmental and Energy Considerations - Excellent SO_2 removal is possible in a simple scrubber. No other pollutants are removed. Na_2SO_3/Na_2SO_4 is not a desirable waste product; disposal may cause serious secondary pollution problems. No additional energy is required to crystallize the products, except for drying. Gas reheat is required, but pressure drop and L/G are relatively low. Sodium carbonate is required as a raw material.

Development Status - The process has been commercially demonstrated on oil-fired boilers in Japan and coal-fired boilers in the U.S. It is offered in the U.S. by Combustion Equipment Assoc., FMC, and others. The process has been fully integrated. It uses commercial technology, and no scale-up problems are expected.

Economic and Technological Considerations - The high cost of Na_2CO_3 makeup may make the process unattractive unless CaO becomes very expensive (high transportation costs), Na_2CO_3 waste is available, low-sulfur coal is being used, or the plant is small. The scrubber system is efficient, but waste disposal can be quite complex.

Applicability - Operating characteristics of the process should not seriously limit its applicability to utility or industrial applications. It can be turned down easily, retrofitted, and modularized. Process sections can be decoupled. Applicability is limited, however, to areas where a cheap, plentiful supply of sodium carbonate is available and where the Na_2SO_3/Na_2SO_4 product can be marketed or disposed of safely. Evaporation ponds may be the only acceptable method of disposal. Because of the expense of sodium carbonate and difficulty of disposing of the waste, the process is also primarily limited to application with low-sulfur Western coal.

Summary and Conclusions - This process scored well compared to other throwaway processes. It is capable of excellent SO_2 removal with low energy requirements, is well developed, can be turned down easily, and is relatively simple overall. Limited availability and high cost of sodium carbonate and difficulty in disposing of the waste product in an environmentally acceptable manner are serious disadvantages, however. These factors generally limit applicability of the process to western locations utilizing low or moderate sulfur coal. However, because of its advantages, the process should be considered further for these applications.

References - AN-147, CA-327, PE-259.

SODIUM HYPOCHLORITE

Process/Subsystem Description - Flue gas is scrubbed by a solution of NaClO and lime at a pH of between 8.5 and 10. About 95% of the incoming SO_2 is absorbed, resulting in the precipitation of gypsum in the scrubbing liquor. The gypsum is centrifuged from the liquor before and after lime addition. The centrifuged liquor is subjected to electrolysis to yield NaClO and $Ca(OH)_2$ in the liquor with the evolution of H_2 gas.

Environmental and Energy Considerations - This process is capable of 95% SO_2 removal. It does not appear to have potential for multipollutant removal. A gypsum product containing traces of NaCl and H_2SO_4 is produced. Disposal of this product (if it cannot be sold) could cause serious secondary pollution problems. Energy requirements are high; pressure drop and L/G are relatively low but reheat is required and electrolytic regeneration requires a large amount of energy. Hydrogen gas which may be of some commercial value is produced by one electrolytic regeneration. NaClO is required as a raw material.

Development Status - A 300 scfm pilot plant was reported to be operational in Japan in 1973. No information has been reported since that time. Apparently the process has not been integrated and makes little use of commercial technology. Scale-up problems could be expected.

Economic and Technological Considerations - Electrolysis of the absorbed ion liquor would probably be costly. In addition, sulfuric acid and NaCl generated by the SO_2 absorption could cause corrosion problems. A source of NaClO would have to be found.

Applicability - The applicability of this process is somewhat limited. It can be turned down and the process sections can be decoupled, but may be difficult to retrofit or modularize. The need to sell or dispose of large quantities of gypsum also limits its applicability.

Summary and Conclusions - This process scored low compared to other throw-away processes. It has a low state of development, and relatively poor applicability. It is also relatively complex and scored below average in environmental and energy considerations. It is capable of good SO_2 removal, but the high energy requirements of the process make commercialization of it improbable. It is not recommended for further eveluation.

References - HA-644

SOIL PROCESS

Preliminary work was done on a process for flue gas desulfurization by soil in 1973 or 1974 by Dr. George E. Klinzing of the University of Pittsburgh. Basic laboratory data were collected and the results were submitted to EPA. Development has ceased due to a lack of funding and the process has not advanced beyond the conceptual stage.

Reference - KL-095

SPRING-NOBEL HOESCHT

Process/Subsystem Description - The flue gas from the boiler is first cooled to 95°F by direct contact with recirculating water which is cooled by heat exchange with cooling water. The flue gas then passes through an absorber where it is contacted with a glyoxalic acid solution which removes the SO_2. The SO_2 rich acid solution is regenerated in a steam stripper and then recirculated to the absorber.

Environmental and Energy Considerations - The SO_2 removal efficiency of this process is greater than 90% but no multipollutant removal effectiveness is expected. Secondary pollutant problems with sulfate formation may exist. Stack gas reheat would be necessary. No reducing gas is needed. The L/G and pressure drop are low for the absorber. Glyoxalic acid is the only major raw material required.

Development Status - The process has been tested on sulfuric acid tail gas in France. It has not been integrated. Except for the nonadiabatic flue gas cooling step, the system uses current technology. Scale-up problems should be encountered only for the gas cooling step.

Economic and Technological Considerations - The potential problems associated with sulfate and chloride removal from the absorbent add some chemical complexity to the process. The mechanical complexity of the process is increased slightly by the materials of design problems associated with nonadiabatic flue gas cooling. Overall, the process is relatively complex mechanically.

Applicability - The applicability of the process to utility and industrial operations should not be limited by any significant problems. Good turndown and retrofit capability should be possible. The SO_2 may be converted and marketed as either sulfur or sulfuric acid. Industrial modularization should be feasible. However, the system is not particularly suited for decoupling absorption from regeneration.

Summary and Conclusions - The Spring-Noble Hoescht process rated average in the evaluation of the wet regenerable FGD processes.

Primary reasons for this rating are limited previous development work, process mechanical complexity, and limited decoupling ability. The process is not recommended for individual evaluation, however, it should be considered as part of the absorption and steam stripping evaluation.

References - ST-409

STONE AND WEBSTER/IONICS PROCESS

Process/Subsystem Description - Flue gas from the boiler is fed to the bottom of an absorber where it is first quenched by circulating water. As the flue gas moves up the absorber it is contacted with a caustic soda solution containing sodium sulfate. Cleaned gases are discharged to the stack. The spent absorbent, now containing sodium sulfite and bisulfite, is mixed with sulfuric acid and pumped through a stripper. Gaseous SO_2 is released out the top of the stripper for recovery. The stripped liquid is conditioned and sent to electrolytic cells for regeneration.

Environmental and Energy Considerations - Excellent SO_2 removal efficiencies with NaOH scrubbing are possible. Multipollutant removal capabilities have not been proven. Secondary pollutant problems are limited to a small dilute sulfuric acid stream which must be disposed of. Stack gas reheat is required, but no reducing gas is needed. The electrolytic cells require substantial quantities of electricity for operation. Pressure drop for the system is not large. Raw materials include sodium carbonate and hydrogen peroxide.

Development Status - The process has been tested on a 2000 cfm coal-fired pilot plant. It was not fully integrated. The system uses current technology; however reliable demonstration has not been proven. Minor scale-up problems may be anticipated.

Economic and Technological Considerations - The chemistry of the SO_2 absorption in the scrubber is simple. That involved with regeneration is somewhat complex, however. Chlorides, particulates, and dissolved iron can cause problems in the cells. The scrubber is simple mechanically. However, a prescrubber is probably necessary for complete particulates and chlorides removal. Regeneration equipment is considered complex mechanically.

Applicability - High sulfur fuels will require larger amounts of electricity for regeneration. The system is easily turned down and decoupled. Modularity should be an asset. Retrofitability should not pose any significant problems.

Summary and Conclusions - The Stone and Webster/Ionics process rated relatively high among the wet regenerable FGD processes evaluated. Primary reasons for its high rating include very good utility applicability and an excellent SO_2 removal efficiency. Advantages of the process include lower raw material requirements than sodium scrubbing systems and simpler sulfate handling than Wellman-Lord. Disadvantages include potential problems with chlorides, particulates, and dissolved iron, but the major disadvantage is the large energy requirement, especially for the electrolytic cells. Although this process received a high numerical rating, it is not recommended for further evaluation because of the high energy requirement for regeneration. It is not felt to offer technological or economic advantages over the Wellman-Lord process which is similar in concept.

References - FE-128, OT-R-051

SULF-X PROCESS

Process/Subsystem Description - The Sul-X process uses a slurry of iron sulfides and water to sorb SO_2 through the reaction of SO_2 and water to produce sulfur and iron hydroxide. The iron sulfides are then regenerated through reaction with carbon (coal) in a thermal regeneration step to produce iron sulfides, CO_2, and sulfur. The sulfur is condensed and the regenerator tail gas is routed to the kiln firebox. Kiln firebox flue gas is sent to absorber for clean up. Regenerated iron sulfide is reslurried and returned to the absorber. The exact process chemistry (in terms of particulates, iron sulfides and intermediates) in the system is proprietary at this time.

Environmental and Energy Considerations - Removal of SO_2 at the 90-98 percent level and simultaneous removal of NO_x are reported by the process developers. A purge stream for chloride removal may be required. Stack gas reheat will be required. The use of coke or coal as a reductant avoids the use of reducing gas, but regeneration energy requirements are still comparable to those for the MgO process. Raw materials supply may be a problem for units not near a source of iron sulfides.

Development Status - The system has been demonstrated at the bench scale and at a 1 Mw plant testing the absorption section. The process has not been operated in an integrated mode to date at any scale. Scale-up problems may be significant. A problem identified in the 1 Mw plant was that of obtaining adequate SO_2 loading in the absorber.

Economic and Technological Considerations - The developers of the process claim competitive capital costs and lower operating costs than existing processes. Factors cited as contributing to this advantage include extensive use of mild steel rather than acid resistant equipment, low power and water requirements; little or no sludge disposal, and recoverable, regenerable or marketable by-products. The process chemistry has been said by the process developer to be very complex. The process also appears to involve a large number of process steps. As with any process of this chemical and mechanical complexity, control problems may be encountered.

Applicability - The system appears to be generally applicable to utility boiler flue gas sources. The developers claim that smaller, simpler equipment can be used with this system, which can be beneficial in space-limited retrofit applications. The process would seem to have fair turndown and decoupling ability.

Summary and Conclusions - The Sulf-X process is a relatively undeveloped process about which little specific information is available. It is chemically complex and could present control problems. The process is claimed to be applicable to NO_x control and to be mechanically simple due to the use of mild carbon steel. Although the process seems to have some potential applicability, the proprietary nature of the basic data make evaluation uncertain. It is recommended that the process be further evaluated due to its potential for simultaneous SO_x/NO_x removal.

References - LE-311, ST-510

SULFURIC AND NITRIC ACID RECOVERY METHOD

Frank Snyder of City Services submitted an unsolicited proposal to EPA on June 29, 1976, based on a theoretical SO_2 removal process. HNO_3 and NO_2 are injected into flue gas to oxidize SO_2 and NO_x to SO_3 and N_2O_3. The gas is then scrubbed with 80% H_2SO_4 at 400°F to generate an $HNSO_5$ solution. Fly ash is recovered, and the solution passed through a carbon filter. The process is still at the conceptual stage, and therefore was not evaluated.

References - Personal Communication

SULFURTAIN PROCESS

Process/Subsystem Description - In the Sulfurtain process, pulverized limestone is intimately mixed with ground coal before combustion. The process was initially developed for use in chain grate stokers and fluidized-bed boilers. For such applications the Sulfurtain mixture is briquetted prior to combustion. More recently, research effort has concentrated on applying the process to pulverized coal-burning boilers. SO_2 is captured by the limestone in the boiler to control flue gas sulfur levels.

Environmental and Energy Considerations - In small scale, 40 minute tests, SO_2 removal increased during the test period, resulting in a removal of 85 percent at the end of the test. In this test burn, in which a coal sample was combusted to completion, average SO_2 removal for the test was 50 percent. Consequently, the process' ability to achieve adequate SO_2 control on a continuous basis remains to be demonstrated. The process does not appear to be capable of removing NO_x or other pollutants. Disposal of the waste solids produced in the boiler could cause secondary pollution problems. In addition, particulate emissions could be increased. Excess limestone could reduce the efficiency of the electrostatic precipitator. Energy would be required for grinding the limestone and mixing it with the coal, but no gas reheat is required and, since there is no scrubber, no energy is required for liquid pumping. Energy requirements should thus be relatively low. Limestone is the only raw material required, but up to three times the stoichiometric quantity must be used.

Development Status - The process has been tested at the bench scale, with a charge of 2.2 lb of treated coal for a 40-minute test. The process has apparently not been tested with required particulate removal that would follow. Commercial technology could be used for the grinding operation. Sulfurtain-treated coal would reportedly be burned in pulverized coal-fired boilers, but modifications would be necessary. Use of three times the stoichiometric amount of limestone, for example would increase solids that must be removed from the boiler by up to 100 percent.

The process developers are currently analyzing data and preparing a publication concerning more recent Sulfurtain process developments. Included will be results of a test of Sulfurtain coal in a commercial size boiler. The process developers said that their information would be available in December 1977 or early 1978.

Economic and Technological Considerations - The chemistry of the process is relatively complex; calcination, sorption, and oxidation apparently occur in the boiler with several possible reactions. The process is also complex mechanically. The reaction of lime with fly ash could cause fouling. Greater quantities of solids will have to be accommodated both in the boiler itself and with bottom ash disposal techniques. ESP performance may also be adversely affected.

Applicability - The process would be turned down with the boiler since the SO_2 sorbent is contained in the coal. There are no process sections that would have to be decoupled. The process should be suitable for industrial modularization. Burning the Sulfurtain-treated coal in existing boilers would probably be difficult, however. The need to dispose of increased quantities of waste could limit applicability.

Summary - This process scored low compared to other throwaway processes. Its applicability would be limited to use with low sulfur coal because of the low SO_2 removal. Burning the Sulfurtain-treated coal in existing boilers would probably be difficult. This process is not recommended for further evaluation.

Reference - BU-281

SUMITOMO HEAVY INDUSTRIES

Process/Subsystem Description - Flue gas is sent to a particulate removal device and heated to reaction temperature (390-450°F) by an in-line heater in retrofit applications. NH_3 is then injected into the flue gas before it enters a moving-bed reactor containing an activated carbon catalyst. The NO_x is converted to N_2 by catalytic reduction with NH_3 and SO_x is absorbed on the catalyst in the form of H_2SO_4 and NH_4HSO_4. The catalyst exiting the bottom of the reactor is sent to a regnerator operating at 660°F. In the regenerator the SO_2 is evolved and the catalyst is regenerated.

Environmental and Energy Requirements - It is claimed that the system may remove 85-90 percent of the NO_x and 95 percent of the SO_x from the flue gas. Some particulate matter is removed by the catalyst bed and must be disposed of. There is a definite potential for secondary air pollution with NH_4Cl and excess NH_3 exiting the stack. The NH_4Cl is formed by the HCl in the flue gas reacting with the injected NH_3.

There is a substantial carbon loss in the regenerator proportional to the SO_x content of the incoming flue gas because the carbon is used to regenerate the H_2SO_4 and some of the NH_4HSO_4 by the action $C + 2H_2SO_4 \rightarrow 2SO_2 + CO_2 + 2H_2O$. Therefore, the process is not recommended for flue gas with a high SO_2 content. Ammonia is required as a raw material in the process. The overall energy requirement for the process is high if the carbon makeup is included as an energy input rather than as a raw material.

Development Status - Development of the process began in 1973. Bench-scale testing was conducted from 1974 to 1975 on flue gas from an oil-fired boiler using a fixed-bed reactor. Pilot testing treating flue gas from a steel mill sintering plant using a moving bed reactor was conducted from October 1976 through March 1977.

Economic and Technological Considerations - The overall process is relatively simple chemically but relatively complex mechanically. A moving bed reactor and an indirectly heated regenerator give the process its mechanical complexity.

Applicability - This system cannot be easily decoupled between the reactor and regenerator because storage of the catalyst between the two process steps would cause a substantial heat loss in the process. In addition solids handling would be greatly complicated by such a decoupling system. The process should follow load changes well. Requirements for absorption at high temperatures may limit retrofitability. Modularization of the process should be possible.

Summary and Conclusions - The Sumitomo Heavy Industries NO_x/SO_x process is the pilot plant stage of development. The process has a potential problem with secondary pollution with unreacted NH_3 leaving with the flue gas. This process is not recommended for further evaluation.

References: FA-149

TAMPELLA RECOVERY PROCESS

Process/Subsystem Description - The Tampella Recovery Process (TRP) is a subsystem that may be used in the regeneration operations of certain FGD systems. It was developed for use in the pulp and paper industry. TRP produces Na_2CO_3 and concentrated H_2S from green liquor (sodium sulfide solution). Clarified green liquor is precarbonated with flue gas to convert Na_2S to NaHS. The precarbonated solution is acidified with $NaHCO_3$ in a steam stripper under vacuum. The NaHS reacts to form H_2S and Na_2CO_3. Moisture is removed from the stripper vapor in a surface condenser, resulting in a stream of concentrated H_2S. Na_2CO_3 monohydrate is crystallized from the stripped green liquor.

Environmental and Energy Considerations - Secondary pollution should not be a problem. All liquid streams are apparently recycled within the system. Energy requirements (steam and electricity consumption) for application of the TRP to FGD systems appear to be high.

Development Status - The TRP, licensed in the U.S. by Babcock and Wilcox, is commercially available for application in the pulp and paper industry. A preliminary engineering study by B&W indicated that TRP technology is suitable for use as the carbonation step of the Atomics International Aqueous Carbonate Process (ACP). A test of the TRP stripper (50 MW equivalent) carried out at Alizay, France, confirmed the technical feasibility of this application. The TRP has not been integrated with the other steps of the ACP, however. Moreover, a carbonation scheme developed by AI for use in the ACP appears to have significantly lower energy requirements than the TRP, although it produces a more dilute H_2S stream than the TRP.

Economic and Technological Considerations - The TRP is relatively complex, chemically and mechanically. Steam and electricity consumption are high, but a concentrated stream of H_2S is produced.

Applicability - The TRP is not generally applicable to FGD systems. It can be used to reduce Na_2S solution (green liquor) to H_2S and Na_2CO_3, and thus is applicable to processes requiring this step, such as the Atomics International Aqueous Carbonate

Process. Its high energy consumption limits its applicability even in this situation, however.

Summary and Conclusions - This subsystem was developed to regenerate Na_2CO_3 from sodium sulfide. Although this process is being used commercially in the pulp and paper industry, it has limited applicability to FGD systems. Energy requirements are high and it is unlikely that this subsystem will be coupled with FGD systems to develop a regenerable process. This process was not recommended for further evaluation.

References - LA-194, OT-R-051

TOPSOE PROCESS

The Topsoe process was developed by Haldor Topsoe, Inc., and Societe-National des Petroles d'Aquitaine (SNPA) for treating tail gas from Claus plants. The tail gas contains compounds such as H_2S, S, and CO which are converted to their oxidized forms by incineration at 1000°F or by a lower temperature catalytic incineration method. The resulting gas stream has an SO_2 concentration of about 1.2 percent, much higher than the concentration in power plant flue gas. The hot gas stream is cooled in a waste heat boiler and then passed through a 2-stage catalytic SO_2 converter with interstage cooling. Most of the SO_2 in the gas is converted to SO_3. The gas is then cooled again, and routed through a 2-stage concentrator-absorber where acid contact is provided. The SO_3 in the gas is absorbed, and 94 percent H_2SO_4 is produced.

The higher SO_2 content (1.2%) in tail gas for which this process was designed makes recovery more economical than it would be for flue gas with lower SO_2 concentrations (0.1-0.3%). The process as developed is not applicable for treating power plant flue gas, and thus was not considered in the evaluation.

References - CA-327, SL-070

TSK SULFIX PROCESS

Process/Subsystem Description - The TSK Sulfix process, developed by Tsukishima Kikai Engineering Company (TSK) in Japan, uses an adaptation of the Billerud process to reduce sodium sulfite obtained in stack gas scrubbing. Stack gas is scrubbed with recycled sodium carbonate solution. Sodium sulfite solution from the scrubber is reduced to H_2S and dry sodium carbonate in an oil burning reactor operating under partial oxidation conditions. A substantial amount of carbon is also formed. The sodium carbonate is collected in an electrostatic precipitator, dissolved, and oxidized to convert the small amount of NaHS formed to thiosulfate. The solution is then filtered and the carbon recycled to the reactor. Because of the low concentration of H_2S in the reactor effluent gas (4-7%), a wet system would probably be used for converting the H_2S to sulfur.

Environmental and Energy Considerations - The process should be capable of excellent SO_2 removal, but there does not appear to be potential for multipollutant removal. A small amount of NaHS may be formed in side reactions. If not oxidized to thiosulfate, the NaHS could decompose in the scrubber and evolve H_2S. Heavy oil is required for regeneration, but the L/G and pressure drop should be relatively low to moderate. Stack gas reheat will be necessary. Raw materials required are sodium carbonate and heavy oil.

Development Status - TSK has done pilot-plant work on the process. The regeneration step adapts commercialized technology to an SO_2 scrubbing application, but the process has not been integrated and significant development work remains. The H_2S conversion process is relatively undeveloped. Scale-up problems may be substantial.

Economic and Technological Considerations - The TSK process is straightforward, but it is complicated by the very dilute stream of H_2S that is produced. This dilute stream makes sulfur recovery difficult. Na_2SO_4 may not be effectively reduced under the relatively mild conditions. Carbon and sodium carbonate may build up in the recovery boiler, which must be periodically removed. The scrubbing step is chemically and mechanically simple, but the regeneration operation is quite complex.

Applicability - The absorption and regeneration steps could be decoupled relatively easily, and the process should not be difficult to retrofit. The by-product should be marketable and the system should be capable of industrial modularization.

Summary and Conclusions - The TSK Sulfix process rated low in the evaluation of the wet regenerable processes. This is due to its relatively undeveloped state and its chemical and mechanical complexity. Other disadvantages of the process include potentially severe secondary pollution problems with H_2S and a fuel oil requirement for regeneration. The process is not recommended for further consideration.

References - HA-651, SL-070, SL-082

TYCO CHAMBER PROCESS

Process/Subsystem Description - The Tyco Chamber Process is a sulfuric acid production process which has been adapted to SO_2 scrubbing. The key concept in the process is the use of NO_2 in the flue gas to oxidize SO_2 to SO_3. The SO_3 forms sulfuric acid in the aqueous scrubbing medium and is removed by scrubbing with recycled sulfuric acid. The sulfuric acid combines with N_2O_3 (which is formed from the reaction of NO and NO_2) to produce nitrosylsulfuric acid ($HNSO_5$). The resulting stream is stripped with a small stream of flue gas; the oxygen in the gas oxidizes the $HNSO_5$ to NO_2 and H_2SO_4. Some of the NO_2 is then absorbed and converted to nitric acid; the rest is recycled to the inlet flue gas stream. The sulfuric acid is sold. The process thus removes NO_2 in addition to SO_2.

Environmental and Energy Considerations - This process conceptually removes NO_x as well as SO_2 with no serious secondary pollutant problems. Energy requirements could be fairly high since the flue gas must pass through a reactor and cooler as well as a scrubber. Also, a catalytic stripper and NO_2 absorber must be operated in addition to the oxidation reactor and SO_3 scrubber. No gas reheat will be necessary, however. Ideally, the process may have very low raw material requirements. In some cases, however, ammonia may have to be added and converted to NO_2.

Development Status - The Tyco process was developed in several small scale experiments under sponsorship of EPA. There is currently little or no development underway. The process is based on commercial technology used in sulfuric acid production, but the composition and temperature of power plant stack gas introduces complications in application of the technology to SO_2 recovery. Scale-up problems would probably be encountered. The oxidation chamber was drastically under-designed even in the small scale test unit.

Economic and Technological Considerations - The chemistry of the process is quite complex and difficult to control, and the equipment required is large. Large amounts of NO_2 must be recycled to the inlet gas stream; efficient removal of NO_x is thus required if a large percentage of the NO_x in the stack gas entering the system is to be recovered.

Applicability - Special construction materials would probably be required to handle the circulating sulfuric acid. Concentrated sulfuric acid is produced as a by-product, along with nitric acid. Retrofits may be difficult since flue gas must be divided and passed through two different scrubbers. In addition, decoupling of the process steps would probably be difficult.

Summary and Conclusions - Although the process was originally felt to possess some potential advantages, experimentation found that equipment requirements were large, and process control was extremely difficult. These problems were deemed insurmountable and development of the process was halted. The process is not recommended for further consideration.

References - SL-070

UNITIKA PROCESS

Process/Subsystem Description - Unitika's system requires that flue gas first pass through a particulate removal device and be heated to 390-480°F before passing through a packed tower containing fixed carbon beds. In new applications, flue gas could be removed from the boiler train at reaction temperature to avoid reheat to 390-480°F. The SO_2 in the flue gas reacts to form several products which are removed by adsorption in the carbon catalyst while the NO_x is reduced by NH_3 to N_2 which is removed with flue gas exiting the reactor. When the carbon bed becomes saturated, it is removed from the process and a regenerated bed is placed on-stream. The carbon is regenerated in the presence of a hot (570-660°F) low-oxygen gas so that the SO_2 is evolved.

Environmental and Energy Requirements - Greater than 90 percent SO_x and NO_x removal is claimed, but a low space velocity is required which means that large absorbers are necessary. Process control must be good to avoid ammonia discharge to the atmosphere. The process requires ammonia and some type of fuel for heating the fuel gas prior to the carbon beds in retrofit applications. Unreacted ammonia leaving with the flue gas is a serious potential secondary pollution problem. A significant amount of fuel is also needed for the regeneration step. The carbon consumption is about 50 percent of total system carbon capacity per year.

Development Status - Unitika began development of an SO_x removal process in 1971. This removal technique with activated carbon was evaluated with two small bench-scale units. When NO_x removal became necessary in Japan, Unitika incorporated NO_x removal into the SO_x removal process. A pilot plant treating about 2650 scfm of flue gas is currently operating in Japan.

Economic and Technological Considerations - This system is fairly simple chemically and complex mechanically. The carbon beds used for absorption must be regenerated fairly frequently and large dampers or valves must be used to direct gas flow. These valves must be specifically designed to withstand this heavy work load. Similar processes using multiple beds that must be valved on and off-line have experienced problems in this area.

Applicability - This process appears to be equally applicable for utility or industrial use. Decoupling of process steps is possible but costs for additional carbon beds could be high. Modularization of the process is possible and turndown can be handled by simply removing absorption beds from use. The process might be difficult to retrofit because of the large absorbers. Reheat requirements in a retrofit application could limit applicability.

Summary and Conclusions - The Unitika NO_x/SO_x process is the pilot plant stage of development. The process has a potential problem with secondary pollution with unreacted NH_3 leaving with the flue gas and appears to offer no advantages over other carbon and copper oxide processes. This process is not recommended for further evaluation.

References - FA-149

UOP SULFOXEL

Process/Subsystem Description - Although a number of aqueous scrubbing media are described in patents issued concerning the Sulfoxel process, sodium compounds were used in the process scheme carried to prototype scale. Cooled flue gas from a water prescrubber is contacted in a wet scrubber by an aqueous solution containing the following sodium compounds: NaSSH, $NaHCO_3$, Na_2CO_3, and Na_2CO_2. A slip stream of the recirculated sodium sorbent is pumped to the regeneration section where the following process steps take place: crystallization, catalyzed reaction with H_2S, separation, catalyzed reduction with CO and steam stripping. Sodium sulfate, H_2S and sulfur are produced in the regeneration section. The H_2S is recycled back to the crystallizer and first reactor. Although the process chemistry is not well defined, it is known that a complex series of oxidation/reduction reactions involving sulfite, bisulfite, thiosulfate, polythionates, sulfides, and hydrogen sulfide, which take place at various stages in the process, result in the production of elemental sulfur.

Environmental and Energy Considerations - The process produces a sizeable waste stream of Na_2SO_4. The reducing gas of mixed hydrogen and CO could be produced from coal, but considerable clean-up would be necessary. Reheat is required, and energy requirements for regeneration are high. No NO_x removal would be achieved, but high SO_2 removal efficiencies (95+%) are possible.

Development Status - The process was developed through the 25 MW prototype scale, but after highly unsuccessful operation the prototype was abandoned. UOP has no plans to continue development work on the process. The process has not been integrated. It appears to require extensive use of new technology. Serious scale-up problems may be encountered.

Economic and Technological Considerations - This wet scrubbing process is quite complex chemically and high temperatures and pressures are required in both catalytic reactions. Capital and operating costs for this process would be very high. Severe scaling problems due to iron compounds in the flue gas fly ash were experienced during the prototype operation.

Applicability - Prototype operation on a utility boiler flue gases was highly unsuccessful. The complexity of this process while offering no advantages over other wet scrubbing processes makes applicability to commercial installations improbable. The process does, however, appear to have capability for retrofit, modularization, and decoupling, but only limited capability for utility turndown.

Summary and Conclusions - This process scored below average compared to other wet regenerable processes. It had low scores for environmental and energy considerations and economic and technical considerations, and average scores for development status and applicability. Because of its chemical complexity and high capital and energy costs, this process is not recommended for further evaluation.

References - CH-406, SL-070

URANIUM OXIDE

Process/Subsystem Description - The Brookhaven National Laboratory has investigated the use of uranium oxide to absorb SO_2 at around 570°F. It would then be thermally regenerated at 930°F to give a 20% SO_2 stream. This could then be used for sulfuric acid or sulfur production.

Environmental and Energy Considerations - The process showed good potential removal of SO_2 but removal of other pollutants was not demonstrated. The loss of UO_2 could be a serious environmental problem. Large amounts of energy would be used in thermal regeneration of the uranium compounds, although gas reheat or reducing gas would not be required.

Development Status - Investigations of the process were not taken beyond bench scale and there is no interest in the process at this time. An integrated system was not run.

Economic and Technological Considerations - Uranium oxide is a difficult material to obtain and loss of such a material would be economically unacceptable. The process would be mechanically complex because of the requirement that these losses be eliminated.

Applicability - The process would probably be applicable to utility or industrial applications. It would, however, probably require batch operation and have limited turn down ability.

Summary and Conclusions - The UO_2 process is undeveloped and there appears to be no chance that it will be developed, principally because of expense of the absorbent and environmental problems associated with its loss. The process is not recommended for further consideration.

References - SL-070

WESTVACO

Process/Subsystem Description - In the Westvaco process, SO_2 is absorbed at 250°F in a fluidized bed as H_2SO_4 on activated carbon. The carbon is regenerated in fluidized bed reactors by a three step operation to give elemental sulfur: $H_2S + H_2SO_4 \rightarrow S$, S stripping, $H_2 + S \rightarrow H_2S$. The temperature in the final step is 1000-1200°F. An optional method of regeneration produces concentrated SO_2 by direct thermal regeneration in the presence of hydrogen.

Environmental and Energy Considerations - Removal of SO_2 in excess of 90 percent has been demonstrated. A recent study has shown the process to have no NO_x removal ability. Attrition of carbon may require particulate removal to avoid emissions. No reheat is required but clean fuel is needed to heat the carbon to 1000°F. H_2 requirements are about 4 moles/mole elemental sulfur or 2 moles/mole SO_2 (for concentrated SO_2). The fluidized bed absorber potentially has a large pressure drop (25-50 inches H_2O).

Development Status - A 300 cfm integrated pilot plant was operated for sulfur production by Westvaco in 1974. Production of concentrated SO_2 was tested briefly at bench scale. The process is offered currently by Catalytic, but no development work is underway at this time.

Economic and Technological Considerations - The fluidized bed absorber may be troublesome at a large scale. Carbon attrition is not a well-characterized phenonemon, so cost of carbon makeup may be significant. However, there should be no chemical consumption of carbon as in the Bergbau-Forschung process. Solids handling may be generally troublesome and the process may be regarded as fairly complex mechanically.

Applicability - The Westvaco process appears to be applicable to both industrial and utility boilers. However, the dependence of the fluidized bed operation on gas flow rates will make turn down a very difficult procedure.

Summary and Conclusions - The Westvaco process is not undergoing further development at this time and its future seems rather uncertain. Major problems include high energy consumption in heating fuel and relatively large hydrogen requirements in the reducing step and scale-up and operation of the fluidized bed absorbers due to mechanical complexity. The process is not recommended for further consideration.

References - AV-011, BA-003, BA-254, HA-402, LU-001, RO-204, ST-293, WE-184

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APPENDIX C

EVALUATION FORMS AND CRITERIA FOR DETAILED PROCESS EVALUATION

The Candidate Processes/Subsystems identified in the first phase of the project were evaluated using the detailed evaluation criteria found in this appendix. In addition, the forms used by the Technical Working Group in evaluating the Processes/Subsystems and in recommending further RD&D options are presented.

INTERAGENCY FGD EVALUATION STUDY

Summary of Detailed Evaluation Criteria for Process/Subsystem Selection

I.	Environmental and Energy Considerations	25 points
	A. Compliance with SO_2 Regulations	(5 points)
	B. Potential for multipollutant control	(3 points)
	C. Secondary pollution problems - air	(2 points)
	D. Secondary pollution problems - water	(2 points)
	E. Secondary pollution problems - solid	(3 points)
	F. Energy Intensiveness	(10 points)
II.	Development Status	15 points
	A. Overall process/subsystem development status	(5 points)
	B. Process/subsystem operations and use of commercialized technology	(5 points)
	C. Process Controllability	(5 points)
III.	Economic and Technological Considerations	35 points
	A. Capital Investment Costs	(15 points)
	B. Annualized Costs	(15 points)
	C. Economic Sensitivity to Technological Factors	(5 points)
IV.	Applicability	25 points
	A. Suitability for Utility Application	(10 points)
	B. Suitability for Industrial Application	(10 points)
	C. Flexibility to provide alternate products	(3 points)
	D. Regional/Site Considerations	(2 points)

INTERAGENCY FGD EVALUATION STUDY

Detailed Evaluation for Process/Subsystems Selection

I. Environmental and Energy Considerations — 25 points

A. Compliance with SO_2 Regulations (5 points)
- 5 - ability to comply with future regulations with high sulfur coals (97%)
- 3 - ability to comply as the future regulations with medium sulfur coals (94%)
- 1 - ability to comply with future regulations with low sulfur coals (80%)

B. Potential for multipollutant control (3 points)
- 3 - significant removal of 1 or more
- 2 - some removal of 1 or more
- 1 - no removal of other pollutants

C. Secondary pollution problems - air (2 points)
- 2 - no air emission problems
- 1 - potential air emission problems
- 0 - major air emission problems

D. Secondary pollution problems - liquid (2 points)
- 3 - no liquid wastes
- 2 - liquid wastes that can be easily treated
- 1 - liquid wastes that require unusual treatment

E. Secondary pollution problems - solid (3 points)
- 3 - no solid wastes
- 2 - solid wastes that can be easily disposed
- 1 - solid wastes that require unusual treatment

F. Energy Intensiveness (10 points)
- Chemical and electrical energy requirements compared with technology currently commercialized or under development
  - 6-10 - lower energy requirements
  - 5 - average energy requirements
  - 1-4 - higher energy requirements

Detailed Evaluation for Process/Subsystems Selection
(Continued)

II. Development Status 15 points

A. Overall Process/Subsystem Development Status (5 points)

- How long has developer studied and worked his process/subsystem?
- How much of the process/subsystem is technically well-known and well founded?
- At what level has it been operated and for how long?
  Bench Scale,
  Laboratory,
  Pilot Plant,
  Small Proto-type,
  Paper Study -
- Have all sections been operated as a chemically or mechanically integral system?

B. Process/Subsystem Operations and use of commercialized Technology (5 points)
5 - operations in common practice
3 - industrially demonstrated
2 - some uncommon methods involved
0 - several unproven processing steps

C. Process Controllability (5 points)
5 - simple process without many sensitive control requirements
3 - simple process with sensitive control requirements
2 - complex process without many sensitive control requirements
0 - complex process with control sensitive requirements

Detailed Evaluation for Process/Subsystems Selection
(Continued)

III. Economic and Technological Considerations 35 points

A. Capital Investment Costs (15 points)

15 - 40% less than median
14 - 30% less than median
12 - 20% less than median
10 - 10% less than median
8 - median
6 - 10% more than median
4 - 20% more than median
2 - 30% more than median
0 - 40% more than median

B. Annualized Costs (15 points)

15 - 40% less than median
14 - 30% less than median
12 - 20% less than median
10 - 10% less than median
8 - median
6 - 10% more than median
4 - 20% more than median
2 - 30% more than median
0 - 40% more than median

C. Economic Sensitivity to Technological Factors (5 points)

5 - little uncertainty in technological factors affecting cost

3 - some uncertainty in technological factors affecting cost

0 - considerable uncertainty in technological factors affecting cost

Detailed Evaluation for Process/Subsystems Selection
(Continued)

IV.	Applicability	25 points
	A. Suitability for Utility Application	(10 points)
	B. Suitability for Industrial Application	(10 points)
	C. Flexibility to provide alternate products	(3 points)
	D. Regional/Site Considerations	(2 points)

IV. Applicability — 25 points

A. Suitability for Utility Application — (10 points)

- Retrofitability
- By-product utilization/marketability
- Separability and process steps
- Load following capability
- Acceptability of processing techniques to the industry

B. Suitability for Industrial Application — (10 points)

- Retrofitability
- By-product utilization/marketability
- Separation of process steps
- Ability for process modularization
- Acceptability of processing techniques to small boiler applications

C. Flexibility to provide alternate products — (3 points)

3 - can produce sulfur or acid
2 - can produce both sulfur and acid with significant modifications
1 - produces either sulfur or acid
0 - produces neither sulfur or acid

D. Regional/Site Considerations — (2 points)

2 - process/subsystem suitable over broad range of applications
1 - process/subsystem suitable only for narrow range of applications

INTERAGENCY FGD EVALUATION STUDY - PRELIMINARY DETAILED EVALUATION RATING FORM

Process/Subsystem Name ____________________ Page 1

CRITERIA	REVIEWER COMMENTS	Point Value	Rating
ENVIRONMENTAL AND ENERGY CONSIDERATIONS Compliance with SO_2 Regulations		5	
Potential for Multipollutant Control		3	
Secondary Pollution Problems - Air		2	
Secondary Pollution Problems - Water		2	

INTERAGENCY FGD EVALUATION STUDY - PRELIMINARY DETAILED EVALUATION RATING FORM

Process/Subsystem Name ______________________________ Page 2

CRITERIA	REVIEWER COMMENTS	Point Value	Rating
Secondary Pollution Problems, Solid		3	
Energy Intensiveness		10	
DEVELOPMENT STATUS Overall Process/Subsystem Development Status		5	
Process/Subsystem Operation and Use of Commercial Technology		5	

INTERAGENCY FGD EVALUATION STUDY - PRELIMINARY DETAILED EVALUATION RATING FORM

Process/Subsystem Name ______________________________ Page 3

CRITERIA	REVIEWER COMMENTS	Point Value	Rating
Process Controllability		5	
ECONOMIC AND TECHNOLOGICAL CONSIDERATIONS Capital Investment Costs		15	
Annualized Costs		15	
Economic Sensitivity to Technological Factors		5	

INTERAGENCY FGD EVALUATION STUDY - PRELIMINARY DETAILED EVALUATION RATING FORM

Process/Subsystem Name ________________________________ Page 4

CRITERIA	REVIEWER COMMENTS	Point Value	Rating
APPLICABILITY Suitability for Utility Application		10	
Suitability for Industrial Application		10	
Flexibility to Provide Alternate Products		3	
Regional/Site Considerations		2	

SUMMARY: EVALUATION OF ADVANCED FGD PROCESSES

	Environmental and Energy Considerations	Development Status	Economic and Technological Considerations	Applicability	Total
Ammonia/IFP					
Atomics International - ACP Process					
Bergbau Forschung Dry Absorption Process					
Calcium Chloride Scrubbing Process					
Chiyoda Thoroughbred 121 Process					
Citrate Buffered Absorption Process					
Dowa Aluminum Sulfate Process					
Integrated Cat-Ox Process					
Kurabo Ammonium Sulfate Process					
Lime/Limestone Wet Scrubbing Process					
Magnesia Slurry Scrubbing Process					
Melamine Process					
RESOX Subsystem					
Shell/UOP Copper Oxide Process					
Sodium Carbonate Throwaway Process					
Sodium/Lime Double Alkali Process					
Sorption/Steam Stripping Process					
Sulf-X Process					
Wellman-Lord Process					

PRIORITIZED RECOMMENDATIONS FOR FGD RD&D OPPORTUNITIES

Recommended Option and Expected Benefit	Steps Necessary to Pursue The Option And Projected Timing to Complete Each Step	Estimated Cost of Pursuing Option

APPENDIX D

PROCESS SUBSYSTEM SUMMARY PAPERS

The technical information which provided a basis for the detailed process/subsystem evaluations is presented in this appendix. The evaluation criteria were applied to the processes/subsystems based upon this information and the evaluator's own judgment in order to identify future RD&D activities.

AMMONIA/IFP PROCESS

The Ammonia/IFP Process consists of wet scrubbing with ammonia combined with a regeneration scheme developed by Institut Francais de Petrole (IFP). The SO_2 absorbed is converted to elemental sulfur by the IFP's "Liquid Claus" Process. The ammonia scrubbing process developed by Catalytic Inc. will serve as the basis of this discussion. A system with a similar process concept developed by Research Cottrell will be discussed under process alternatives.

The Ammonia/IFP Process can be divided into four major processing areas, as illustrated in the flow diagram in Figure 1. They are SO_2 absorption, spent brine reduction, sulfur production, and ammonia separation and recycle.

Flue gas is first scrubbed in a venturi humidifier/cooler to remove $HC\ell$ and to adiabatically saturate the flue gas. The saturated flue gas then enters a staged absorber where SO_2 is absorbed in a solution of aqueous ammonium sulfite and bisulfite by the following reactions:

$$SO_2 + (NH_4)_2SO_3 + H_2O \rightarrow 2NH_4HSO_3 \quad (1)$$

$$SO_3 + (NH_4)_2SO_3 \rightarrow (NH_4)_2SO_4 + SO_2 \quad (2)$$

$$O_2 + 2(NH_4)_2SO_3 \rightarrow 2(NH_4)_2SO_4 \quad (3)$$

Each stage in the absorber has a separate liquid feed, effluent stream, and a mist eliminator. The concentration of ammonia salts in the liquor is highest in the lower stages, where most of the SO_2 removal takes place. Ammonia from the regeneration section is primarily introduced into the mixing tanks for the first and second stages. To lower the potential for forming an ammonia plume, the final stage is operated with a low concentration of ammonia salts. No SO_2 is removed in the final stage.

Concentrated liquor from the bottom stage mixing tank is drawn off for regeneration. This spent brine is heated to 300°F in a steam-heated forced circulation evaporator where it is decomposed by the following reactions:

$$(NH_4)_2SO_3 \rightarrow 2NH_3 + H_2O + SO_2 \quad (4)$$

$$NH_4HSO_3 \rightarrow NH_3 + H_2O + SO_2 \quad (5)$$

In addition to the primary products, elemental sulfur, thiosulfate, thionates, and other nonvolatile sulfur compounds are produced by disproportionation.

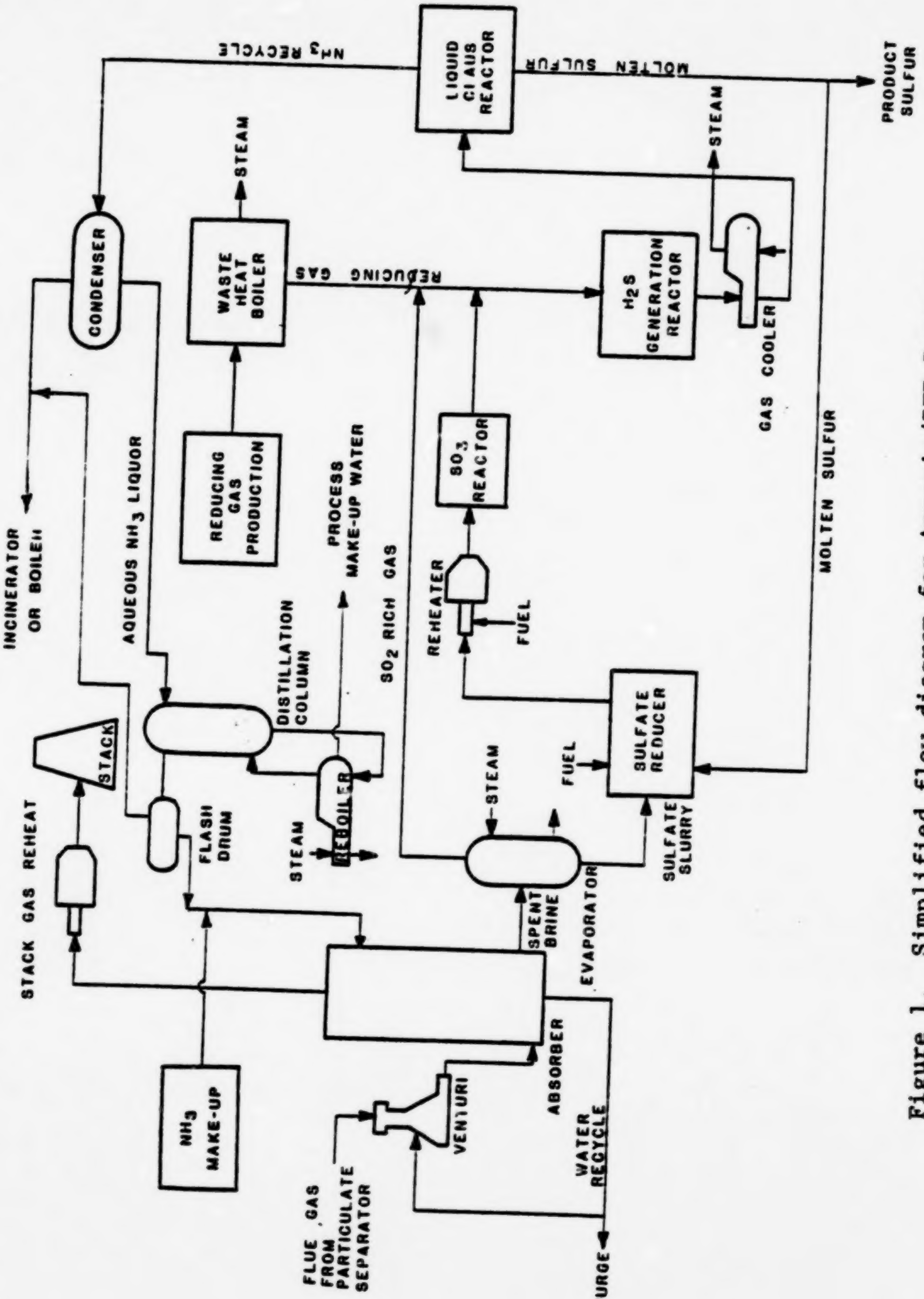
NH3 RECYCLE
LIQUID CLAUS REACTOR
MOLTEN SULFUR
PRODUCT SULFUR
CONDENSER
WASTE HEAT BOILER
STEAM
REDUCING GAS
H2S GENERATION REACTOR
STEAM
GAS COOLER
TO INCINERATOR OR BOILER
AQUEOUS NH3 LIQUOR
REDUCING GAS PRODUCTION
PROCESS MAKE-UP WATER
SO3 REACTOR
SO2 RICH GAS
REHEATER
FUEL
MOLTEN SULFUR
STACK
STACK GAS REHEAT
DISTILLATION COLUMN
FLASH DRUM
REBOILER
STEAM
STEAM
FUEL
SULFATE REDUCER
SULFATE SLURRY
SPENT BRINE
EVAPORATOR
NH3 MAKE-UP
ABSORBER
VENTURI
FLUE GAS FROM PARTICULATE SEPARATOR
WATER RECYCLE
PURGE

Figure 1. Simplified flow diagram for Ammonia/IFP Process.

The vapor produced is ultimately combined with the output of the sulfate reducer and fed to the H_2S generation reactor.

The salt slurry from the evaporator bottom contains sulfates since they do not decompose at the operating conditions of the evaporator. The concentrated sulfate slurry is fed to the sulfate reducer where the sulfates are decomposed under conditions of high temperature (600-700°F) and a reducing atmosphere. A sulfur or sulfur compound acting as a reducing agent is also present. The following reactions occur:

$$(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3 \quad (6)$$

$$2NH_4HSO_4 + S \rightarrow 3SO_2 + 2H_2O + 2NH_3 \quad (7)$$

Reaction heat is provided by an oxygen-starved submerged combustor which bubbles hot gases up through the melt. A small amount of SO_3 is also formed during decomposition of the ammonium sulfate. The SO_3 is reduced to SO_2 by heating and then catalytically reacting it with H_2 and CO reducing gas.

Overhead vapor from the forced circulation evaporator, gas from the SO_3 reduction reactor, combustion products from a heater burning low-Btu gas to provide heat for the reactions, and a reducing gas stream are fed to the H_2S generation reactor. H_2S is generated by the following catalytic reactions at about 900°F:

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O \quad (8)$$

$$SO_2 + 3CO + H_2O \rightarrow H_2S + 3CO_2 \quad (9)$$

Product gas is cooled in a waste heat boiler and then fed to the "Liquid Claus" reactor. The H_2S-SO_2 feed is reacted at a relatively low temperature in a catalyzed organic solvent to produce elemental sulfur. A ratio of H_2S to SO_2 slightly greater than 2:1 must be maintained in the feed stream to the sulfur production unit for successful conversion to elemental sulfur.

The overhead stream from the liquid Claus unit is sent to a condenser for initial separation of NH_3 and water from the noncondensables. The noncondensable gases, which include COS and H_2S, are burned in a tail gas incinerator or in the boiler. The aqueous condensate is purified in a distillation column.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - The Catalytic/IFP Process can easily achieve SO_2 removal efficiencies greater than 90 percent. Removal efficiencies of up to 99 percent can be achieved by adding more stages to the absorber.

Multipollutant Control - Most of the particulate matter remaining in the flue gas after the electrostatic precipitator will be removed. Chlorides are removed in the prescrubber. The process does not appear to have potential for NO_x removal.

Secondary Pollution Problems; Air - Formation of an ammonia salt plume is a serious secondary air pollution problem with most ammonia scrubbing processes. Catalytic has developed a patented "fumeless" technology for operation of the absorber, using control strategy and process instrumentation. Catalytic reports that they have successfully operated a bench-scale unit in a "fumeless" mode and can predict the onset of fuming, but the "fumeless" technology has not been demonstrated on a large scale. The ability of the process to prevent plume formation in a large scale installation remains unproven. Toxic COS and H_2S gases are produced in the sulfur production portion of the process, but can be controlled by burning the gases in the boiler or in a tail gas incinerator.

Secondary Pollution Problems; Water - A purge stream containing chlorides and fly ash is discharged from the venturi prescrubber. This stream, which is about 10 percent of the recycle liquid, is neutralized with lime and sent to the ash pond for disposal. This purge stream should not present serious disposal problems.

Secondary Pollution Problems; Solids - The only solid wastes from the process appear to be the small amounts of fly ash filtered from the scrubber solution by the brine filter. This should not present serious disposal problems.

Energy Intensiveness - This process is relatively energy intensive in that it consumes 170.4 MM Btu/hr of coal for reducing gas production, 60.9 MM Btu/hr of coal for low-Btu gas production to be used as fuel, and 137.7 MM Btu/hr of steam for reheat, the spent brine evaporator, and for the reboiler on the ammonia liquor distillation column. A heat credit of 35.4 MM Btu/hr of steam is produced from the reducing gas production unit and H_2S generation reactor, but this still gives an overall coal and steam requirement of 333.6 MM Btu/hr. Raw material and energy requirements for this process are presented in Table 1.

TABLE 1. RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE CATALYTIC-IFP-AMMONIA SCRUBBING SYSTEM

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (dry)

Raw Materials		
Lime	(lb/hr)	1800
Ammonia, anhydrous	(lb/hr)	110
Polyethylene glycol	(lb/hr)	15.6
Coal	(tons/hr)	8.1
Utilities		
Process water	(10^3 gal/hr)	364
Coal	(10^6 Btu/hr)	60.9
Electricity	(kw)	13250
Steam	(10^6 Btu/hr)	137.7
Heat credit	(10^6 Btu/hr)	35.4

DEVELOPMENT STATUS

Overall Status - Catalytic has demonstrated their "fumeless" technology at the bench scale in a four-inch diameter four stage absorber. The scrubbing process was also tested at a 2 Mw unit on a coal-fired industrial boiler in Calvert City, but did not clearly demonstrate fumeless operation.

IFP has built three ammoniacal brine recovery process installations. The only fully integrated unit is a 25 Mw installation located at the Champagne EDF (Electricite´ de France) power plant in France. The IFP process has not been integrated with a Catalytic absorber, however. In addition, the use of a coal based reducing gas remains to be demonstrated.

Use of Commercialized Technology - In general, commercial technology is used in the regeneration section. The liquid Claus unit for sulfur production is commercially available. New technology would, however, be required for the absorber, to control fume formation and for the reduction section to use a coal-based reducing gas.

Process Controllability - Process control necessary to achieve fumeless operation would be difficult to maintain. To prevent fuming, HCℓ must be removed from the flue gas before it contacts the ammonia, and the partial pressures of NH_3, SO_2, and H_2O must be maintained at such levels that ammonium salts do not form in the gas phase. The absorption tower is designed to remove SO_2 from the flue gas in the lower stages and ammonia and other volatiles from the cleaned gas in the upper stages. A minimum of weepage and entrainment and semi-independent operation of each stage is required to prevent fuming.

Oxidation in the scrubber is important because of its impact on the sulfate reducer. Increased oxidation generates more sulfates and, therefore, a greater energy requirement for the sulfate reducer.

Control of the sulfate reducer may also be difficult. A relatively constant heat rate should be maintained in the sulfate reducer. The submerged combustor may be difficult to control, and may be replaced by an electric induction furnace.

The H_2S generator must be designed and controlled to produce a 2:1 ratio of H_2S to SO_2 in the feed gas to the Claus reactor for successful conversion to elemental sulfur. Possible effects of impurities that may be present in reducing gas produced from coal on the catalysts in the SO_3 reduction-reactor and the H_2S generator are unknown.

ECONOMIC AND TECHNOLOGICAL FACTORS

Analysis of the Catalytic-IFP Ammonia Process indicated total capital costs to be about $92 million. Direct operating costs were estimated to be $9.3 million less $1.5 million for sulfur sales. Unit revenue requirements were estimated at 6.47 mills/kwh using a utility financing method. The process is fairly well developed and processing costs seem relatively insensitive to technological factors. However, costs associated with the absorber may vary depending upon the degree of control that must be taken to prevent ammonia fuming. A summary of capital and operating costs for the Catalytic-IFP Ammonia Process is presented in Tables 2 and 3.

APPLICABILITY

Suitability for Utility Application - The process can be retrofitted into existing units if sufficient space is available. The staged absorber with separate liquid circulation for each stage may require more space than conventional absorbers, however. The system can be turned down to follow boiler load, but care must be taken to avoid weeping of solution between stages of the absorber at low gas loads. This problem can be solved by the use of valve tray absorbers.

The regeneration section can be decoupled from the absorption section by providing storage tanks between the two sections. The sulfur produced as a by-product is marketable. The process

TABLE 2. CATALYTIC-IFP-AMMONIA PROCESS TOTAL CAPITAL INVESTMENT ANALYSIS[a]

	Investment, $
Direct Investment	
Ammonia scrubber (venturi cooler, ammonia scrubber, flue gas reheater, soot blowers, tanks, agitators, bin, filter blowers, feeder, slaker, thickener tank and mechanism, fans, pumps, ductwork)	17,413,000
Claus gas preparation	11,661,000
Claus reaction and ammonia recovery	7,667,000
Gasification	9,226,000
Subtotal	45,967,000
Services, utilities, and miscellaneous	2,758,000
Total direct investment	48,725,000
Indirect Investment	
Engineering design and supervision	3,895,000
Architect and engineering contractor	974,000
Construction expense	6,292,000
Contractor's fees	1,805,000
Total indirect investment	12,966,000
Contingency	12,338,000
Total fixed investment	74,029,000
Other Capital Charges	
Allowance for startup and modifications	7,403,000
Interest during construction	8,884,000
Total depreciable investment	90,316,000
Land	18,000
Working capital	1,563,000
Total capital investment	91,897,000

[a] Basis: New 500 Mw coal-fired power unit (30 yr. life).
Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).
Coal properties: 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Investment requirements for disposal of fly ash excluded.
90% SO_2 removal.

TABLE 3. CATALYTIC-IFP-AMMONIA PROCESS
TOTAL ANNUAL REVENUE REQUIREMENTS ANALYSIS - REGULATED UTILITY

	Annual quantity	Economics[a] Unit cost, $	Total annual amount, $
Direct Costs			
Raw materials			
Lime	6,300 tons	48.00/ton	302,400
Ammonia, anhydrous	385 tons	200.00/ton	77,000
Polyethylene glycol	54.6 tons	800.00/ton	43,700
Coal	56,784 tons	25.00/ton	1,419,600
Total raw materials cost			1,842,700
Conversion			
Operating labor and supervision	35,000 man-hr	12.50/man-hr	437,500
Utilities			
Coal	20,300 tons	25.00/ton	507,500
Steam	964,000 MM Btu	2.00/MM Btu	1,928,000
Heat credit	247,500 MM Btu	-1.25/MM Btu	(309,400)
Process water	2,548,000 M gal	0.06/M gal	152,900
Electricity	92,755,000 kwh	0.029/kwh	2,689,900
Maintenance, 4% of direct investment			1,949,000
Analyses	9,160 man-hr	17.00/man-hr	155,700
Total conversion costs			7,511,100
Total direct costs			9,353,800
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6.0% of total depreciable capital investment			5,419,000
Average cost of capital and taxes at 8.6% of total capital investment			7,903,100
Overhead			
Plant, 50% of conversion costs less utilities			1,271,100
Administrative, 10% of operating labor			43,800
Marketing, 10% of sales revenue			150,300
Total indirect costs			14,787,300
Gross annual revenue requirements			24,141,100
By-Product Sales Revenue			
Sulfur	33,400 long tons	-45.00/long ton	(1,503,000)
Total annual revenue requirements			22,638,100

	Dollars/ton coal burned	Mills/kwh	Costs/million Btu heat input
Equivalent unit revenue requirement	15.09	6.47	71.86

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[a] Basis: New 500 Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up).
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned, 1,500,100 tons/yr, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Total capital investment, $91,897,000; total depreciable investment, $90,316,000; total direct investment, $48,725,000.
Investment and revenue requirements for disposal of fly ash excluded.
90% SO_2 removal; wet venturi particulate removal.

may not be acceptable to the utility industry because of the complex control requirements necessary to prevent plume formation.

Suitability for Industrial Application - Considerations affecting retrofits, decoupling ability, and by-product marketability for industrial application are comparable to those discussed for utility application. The process should be adaptable for modularization. Because of the large number of operations required for regeneration, the process may not be desirable for small boilers except in applications where a central regeneration system could be used for several small scrubber modules.

Flexibility to Provide Alternate Products - This process produces elemental sulfur in a liquid Claus sulfur production unit. The H_2S required for the conversion is produced from the reaction of a gasification product reducing gas with SO_2 produced from the decomposition/reduction of the ammonium sulfite and sulfate compounds. It would be difficult to produce sulfuric acid from the SO_2 stream because the feed gas would contain about 12 percent NH_3, 8 percent SO_2, 62 percent H_2O, and some H_2, CO, and sulfur vapor. The ammonia would be difficult to separate from the SO_2 stream and the H_2, CO, and sulfur vapor would have to be oxidized to H_2O, CO_2, and SO_2. Then the gas would have to be dried in order that 98 percent sulfuric acid could be produced. The combination of these three steps that are required for the preparation of an acid plant feed gas make the Catalytic/IFP process not well suited for acid production.

Regional/Site Considerations - There appear to be no specific regional considerations that would limit applicability of the process.

PROCESS ALTERNATIVES

Research Cottrell - Research Cottrell has proposed an ammonia scrubbing process using the IFP regeneration scheme. The Research Cottrell/IFP Process is similar to the Catalytic/IFP Process, except that Research Cottrell uses a wet electrostatic precipitator following the absorber to control any ammonia fume that is formed. Use of the wet ESP would add to capital and operating costs in the system, but would eliminate the need for sensitive control to avoid plume formation required in the Catalytic Process. This is a proposed design and development work has apparently not gone beyond the conceptual stage.

Elimination of Sulfate Reducer - The sulfate reducer can be eliminated if sulfates are removed as crystallized ammonium sulfate. The process would thus be simplified somewhat and energy consumption would be reduced, but ammonia consumption would be increased and the ammonium sulfate would have to be sold or disposed of.

SUMMARY

The Ammonia/IFP Process uses an aqueous solution of ammonium sulfite/bisulfite to absorb SO_2. Elemental sulfur is produced as a by-product in a "Liquid Claus" reactor. Fume formation is a serious problem with most ammonia scrubbing processes. Catalytic has developed an ammonia scrubbing process that uses a staged absorber with careful process control to prevent formation of an ammonia plume. This "fumeless" operation remains to be demonstrated on a large scale, however. The IFP regeneration scheme has been relatively well demonstrated, but has not been integrated with a Catalytic absorber. In addition, the regeneration is relatively complex. Reducing gas is required to reduce SO_3 formed to SO_2 and to generate H_2S. Use of a coal-based reducing gas may be possible, but has not been demonstrated. The major disadvantage of the process is the possibility of ammonia plume formation, which may occur in spite of complex process control exercised in an attempt to avoid it.

References - EN-125, EN-269, HA-353, HA-419, NA-248, OT-051, RE-151, SL-070, TE-188.

ATOMICS INTERNATIONAL AQUEOUS CARBONATE PROCESS

The Atomics International Aqueous Carbonate Process (ACP) uses an aqueous sodium carbonate (Na_2CO_3) solution to sorb SO_2 from flue gas in a spray dryer. The dry scrubber product is treated to regenerate the scrubbing solution and to produce elemental sulfur.

The ACP can be divided into five major processing areas. These are gas cleaning, reduction, quenching and filtration, carbonation, and sulfur production.

The gas cleaning subsystem consists of the SO_2 scrubbing and product collection equipment. Before the gas enters the scrubber, the ash content must be reduced to 1.0 gr/scf or less to limit the size of the ash removal equipment in the regeneration section. The following reactions occur in the scrubber.

$$SO_2 + Na_2CO_3 \rightarrow Na_2SO_3 + CO_2 \tag{1}$$

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \tag{2}$$

$$SO_3 + Na_2CO_3 \rightarrow Na_2SO_4 + CO_2 \tag{3}$$

Reaction (1) is the primary reaction for SO_2 removal. The spent reactant is entrained as dry particles, which are removed in the product collection cyclones and the electrostatic precipitator.

The dry product collected in the gas cleaning system is conveyed to the reducer. The reducer vessel contains a pool of molten salts at temperatures between 1700 and 1900°F. Carbon is injected into the salt pool in the form of petroleum coke or coal. Combustion air is bubbled through the melt. The following reactions occur:

$$Na_2SO_{3(\ell)} + {}^3/_2C_{(s)} \rightarrow Na_2S_{(\ell)}\ {}^3/_2\ CO_{2(g)} \tag{4}$$

$$Na_2SO_{4(\ell)} + 2C_{(s)} \rightarrow Na_2S_{(\ell)} + 2CO_{2(g)} \tag{5}$$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{6}$$

The mechanism for reactions (4) through (6) is quite complex, involving sequential oxidation-reduction of the sulfur-containing salts. The exothermic reaction (6) provides heat for the endothermic reactions (4) and (5) and for system heat losses. The sodium sulfide melt is dissolved in solution near its boiling point, forming green liquor. This liquor is filtered and then contacted with the CO_2-rich reducer off gas in a series of carbonation towers. The products from the towers are a concentrated Na_2CO_3 solution for recycle to the gas cleaning system and an H_2S-rich gas for feed to a Claus plant. A simplified flow diagram for the ACP is given in Figure 1.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - The ACP can be designed to remove 90 to 95% of the SO_2 from inlet flue gas under normal operating conditions.

Multipollutant Control - SO_2 is removed by reaction with dry Na_2CO_3 powder in the spray dryer and electrostatic precipitator. Particulates are removed in the cyclones and electrostatic precipitator. Fine fly ash particles tend to agglomerate with the atomized droplets in the spray dryer and can be removed with the spent absorbent. The process does not appear to have potential for NO_x removal.

Secondary Pollution Problems; Air - Fugitive emissions of H_2S are possible. These should not present a serious problem. Particulates may be emitted from the product recovery area.

Secondary Pollution Problems; Water - A purge stream of chlorides and possible trace contaminants adsorbed in the spray dryer is discharged with the cooling tower water in the reduction section. This purge stream could raise the concentration of total dissolved solids in the effluent cooling water by an estimated 250 ppm. This water could possibly be used for sluicing ash.

Secondary Pollution Problems; Solids - Wet filter cake from the ACP should not have significant environmental impact. Atomics International has proposed to add this cake to the normal fly ash disposal system used by the power plant.

Energy Intensiveness - The raw material and utility requirements for the ACP are given in Table 1. These figures are based on projections made by AI personnel in their statement of qualifications to EPA (RO-158).

The major raw materials required by the ACP are Na_2CO_3 and petroleum coke. AI regards the availability of petroleum coke as high, especially on the East or West Coast or any area with a high concentration of refinery operations. The possibility of using coal in place of coke would be attractive if delivered coke costs were excessively high. The energy requirements are calculated for the AI carbonation process. If the Tampella Recovery Process were used instead, the steam and electricity required for carbonation would be increased. The ACP should be less energy intensive than many other regenerable processes. It produces sulfur without the use of a reducing gas, and may not require stack gas reheat.

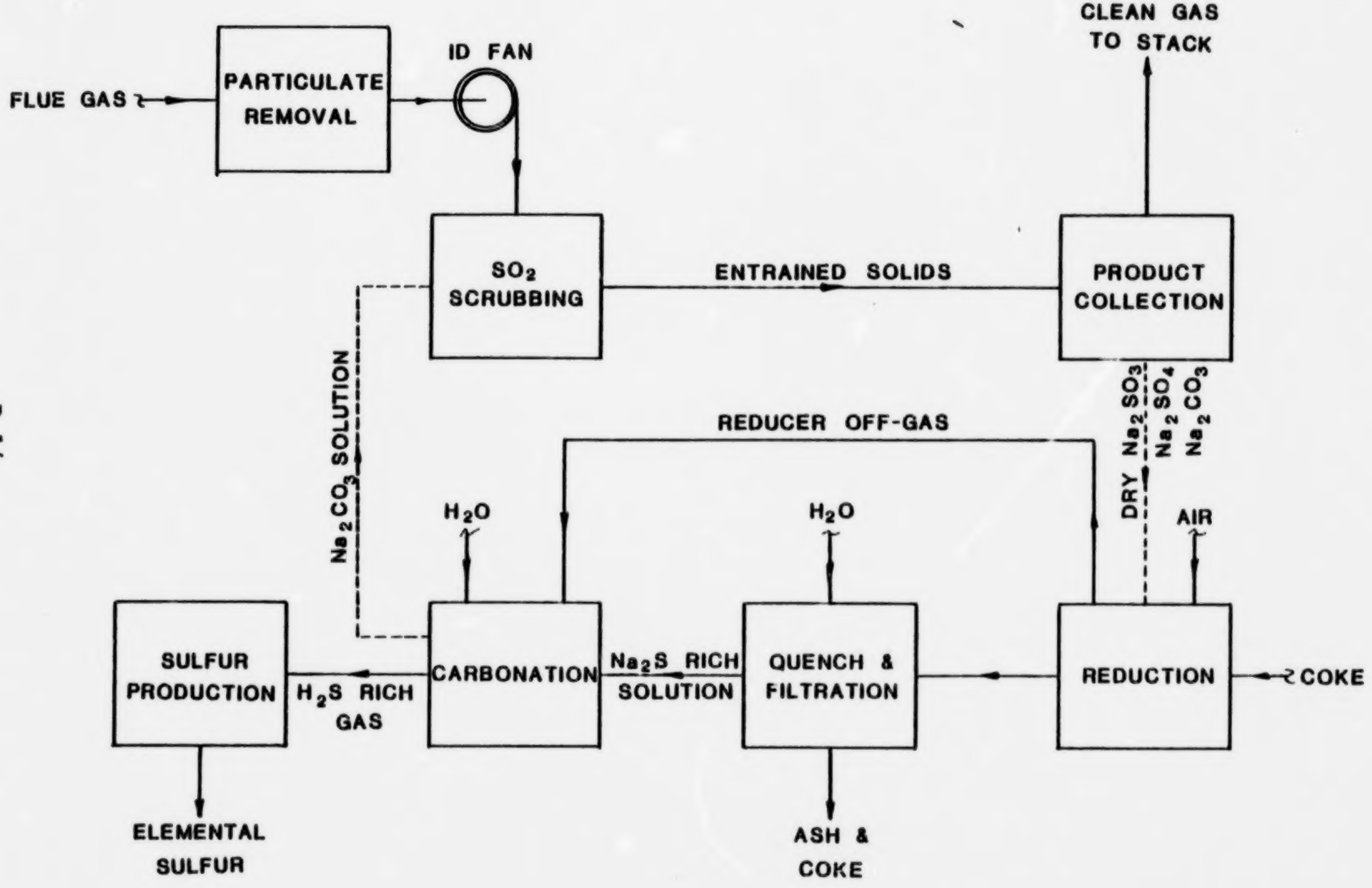
FLUE GAS
PARTICULATE REMOVAL
ID FAN
SO$_2$ SCRUBBING
ENTRAINED SOLIDS
PRODUCT COLLECTION
CLEAN GAS TO STACK
DRY Na$_2$SO$_3$ Na$_2$SO$_4$ Na$_2$CO$_3$
AIR
REDUCTION
COKE
REDUCER OFF-GAS
Na$_2$CO$_3$ SOLUTION
H$_2$O
CARBONATION
H$_2$O
QUENCH & FILTRATION
Na$_2$S RICH SOLUTION
ASH & COKE
H$_2$S RICH GAS
SULFUR PRODUCTION
ELEMENTAL SULFUR

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR ATOMICS INTERNATIONAL AQUEOUS CARBONATE PROCESS

TABLE 1. RAW MATERIALS AND UTILITY REQUIREMENTS FOR THE AQUEOUS CARBONATE PROCESS

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (dry)

Raw Materials	
Na_2CO_3 (lb/hr)	960
Coke (lb/hr)	14,000
Utilities	
Process Water (10^3 gal/hr)	21
Treated Water (10^3 gal/hr)	3.8
Cooling Water (10^3 gal/hr)[1]	258
Electricity	
Gas Cleaning (kw)	8,100
Reduction, Quench, Filtration (kw)	930
Carbonation (kw)	910
Sulfur Production (kw)	620
No. 6 Fuel Oil (10^3 gal/hr)	0.23
Steam - H.P.	
Reduction, Quench, Filtration (lb/hr)	3,500[2]
Carbonation (lb/hr)	36,500[2]
Sulfur Production (lb/hr)	40,000[3]

[1] Cooling water is considered as process water for economic estimates.

[2] Utility Required

[3] Utility Produced

DEVELOPMENT STATUS

Overall Status - Development of the ACP has been underway since 1972. All of the process steps have been tested on a 1000 scfm scale or are considered proven technology by Atomics International. The spray dryer has been tested on pilot units at Bowen Engineering's North Branch, New Jersey facility and at Southern California Edison's Mohave Station. Early bench scale work on the molten salt regeneration unit was performed at AI test laboratories in 1973. Based on this work, pilot scale tests were conducted with a feed rate equivalent to 1.25 Mw. Bench scale tests have also been conducted to determine the feasibility of using coal as the carbon source in the reducer. A fully integrated ACP system has never been operated, however. A 100 Mw demonstration plant is planned for start-up in 1978.

Use of Commercialized Technology - Several of the process steps in the ACP utilize existing technology, but technology for absorption, reduction, and carbonation is still being developed.

Production of elemental sulfur from H_2S is standard Claus technology. The design of the cyclones and electrostatic precipitator in the particulate collection system is considered standard industrial practice, and the technology for the quench and filtration steps is well developed from use in the pulp and paper industry. Carbonation technology has also been developed, but Atomics International is developing a proprietary carbonation process since most of the available commercial processes feature high energy and steam consumption. Spray dryers of the size required for the ACP have been built for applications other than SO_2 absorption. Technology for the use of a spray dryer for SO_2 absorption is still under development. The molten salt reducer utilizes new technology being developed by AI.

Process Controllability - Control of the spray dryer may be difficult. Enough water must be added for good atomization, but the amount of water added should be minimized so that gas reheat is not required. The gas temperature in the scrubber must be kept about 20°F above the dewpoint to prevent condensation in downstream equipment and to produce a dry product for collection. Control of the reducer may also be difficult; historically, the operation of molten salt beds under reducing conditions has been difficult to control. Careful control is required in the quench/dissolver to avoid explosive conditions. The melt must be broken up and dispersed into fine droplets, and the green liquor should be maintained at or near its boiling temperature to avoid rapid pressure increases. Filtration of fly ash and other solids from process liquors has caused problems in other alkali scrubbing systems. This problem is complicated in the ACP by the effect of high temperature reduction on the filtering characteristics of ash and unreacted coke. Tests have shown that fly ash and fuel ash interact with other melt constituents to significantly alter their physical and chemical properties upon quenching.

Because an entire ACP system has not been operated in integrated fashion, the possible effect of contaminants from one area on another is unknown. The impurities introduced with fly ash, coke, or coal in the gas cleaning and reduction areas are of particular concern. These impurities might recrystallize in downstream equipment and cause plugging.

ECONOMIC AND TECHNOLOGICAL FACTORS

Estimated capital and operating costs for the ACP are given in Tables 2 and 3, respectively. Capital costs for the AI process have been estimated at $55,180,000 with unit revenue requirements of 3.99 mills/kwh based on a utility financing method. Since certain areas of the process use technology that is not commercial, there is uncertainty in the cost of equipment and raw materials for these areas. Choice of the carbonation process and reductant also affects costs. The AI carbonation process has much lower energy requirements than other available carbonation processes, but produces a more dilute H_2S stream for feed to the Claus plant. Coal is a cheaper and more readily available reducing agent than petroleum coke, but the ash and other impurities in the coal may cause problems in other areas of the regeneration subsystem.

APPLICABILITY

Suitability for Utility Application - The ACP may be difficult to retrofit to an existing plant because of space requirements. Due to low gas velocities maintained in the spray dryers, the scrubbing vessels are large (on the order of 42 ft. in diameter). Ground space requirements for the regeneration section are less critical for retrofit applications since this equipment could be located in a peripheral plant area, or completely off-site. There appear to be no technical factors other than ground space requirements that limit the application of the ACP to new or existing coal-fired power plants.

Turndown of the spray dryer and product collection equipment is reported to be very good. Simple operation also provides for quick response times. As gas rate decreases, the scrubber liquid feed rate is decreased in direct proportion. Turndown ratios as high as 4 to 1 have been demonstrated with a single scrubber without loss of removal efficiency. For a large installation with 4 scrubbing modules, system turndown as high as 16 to 1 could be possible. The regeneration subsystem is decoupled from the gas-cleaning subsystem by providing for storage of the dry product and regenerated scrubbing solution. The preferred operating mode for the reducer is either 100% capacity or standby. Wide swings in melt temperature should be avoided to prevent spalling of the refractory lining. To compensate for vessel heat losses and maintain operating temperature during standby operation, approximately 400 lb/hr of carbon in excess of the normal absorbent-to-carbon ratio is required. Turndown of the carbonation equipment is compatible with the rest of the regeneration scheme.

Possible corrosion problems and the possibility of embrittlement and cracking affect the choice of materials of construction for the ACP. The reducer is a carbon steel vessel lined with 8-inch thick Monofrax, a refractory brick made of high density alumina which is resistant to the corrosive effects of the melt. Thick-walled carbon steel is preferred for the quench/dissolver to prevent embrittlement and cracking. A 316 stainless steel is used to construct the carbonation columns. The sulfur produced as a by-product should be marketable. Because of the complexity of the process, it may not be as acceptable to the utility industry as some other processes.

Table 2

Atomics International Aqueous Carbonate Process

Total Capital Investment Analysis[a]

	Investment, $
Direct Investment	
Raw materials handling and preparation (rail car unloading system, tanks, agitators, hoppers, blowers, pumps)	707,000
Particulate scrubbing (cyclones, preheaters)	3,064,000
SO_2 scrubbing and product collection (tank, pumps, spray dryers, cyclones, electrostatic precipitators, and carbonate transfer, storage, and feed systems)	11,006,000
Fans (4 fans including exhaust gas ducts and dampers between fan and stack gas plenum)	1,146,000
Reduction (reducers, compressors, tanks, agitators, particulate scrubbers, exhausters, reducer-recuperators, waste heat boiler, burner, solids collection, and feed system, condensers, and smelt spouts)	4,248,000
Carbonation (heat exchangers, hydrocyclone, filters, tanks, precarbonator column, coolers, crystallizers, agitators, carbonators, heat exchangers, condensers, reboilers, exhausters, and pumps)	3,133,000
Sulfur production and storage (Claus plant and storage for 30 days' production of sulfur)	3,765,000
Subtotal	27,069,000
Services, utilities, and miscellaneous	1,624,000
Total direct investment	28,693,000
Indirect Investment	
Engineering design and supervision	2,350,000
Architect and engineering contractor	588,000
Construction expense	4,054,000
Contractor's fees	1,231,000
Total indirect investment	8,223,000
Contingency	7,383,000
Total fixed investment	44,299,000
Other Capital Charges	
Allowance for startup and modifications	4,430,000
Interest during construction	5,316,000
Total depreciable investment	54,045,000
Land	21,000
Working capital	1,164,000
Total capital investment	55,230,000

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[a] Basis:

New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).
Coal properties: 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Investment requirements for disposal of fly ash excluded.
90% SO_2 removal.

Table 3
Atomics International Aqueous Carbonate Process

Total Annual Revenue Requirements Analysis[a]

	Annual quantity	Unit cost, $	Total annual amount, $
Direct Costs			
Raw materials			
Soda ash	3,360 tons	90.00/ton	302,400
Coke	49,100 tons	32.00/ton	1,571,200
Catalyst			41,000
Total raw materials cost			1,914,600
Conversion costs			
Operating labor and supervision	40,000 man-hr	12.50/man-hr	500,000
Utilities			
Fuel oil (No. 6)	1,586,000 gal	0.40/gal	634,400
Process water	1,967,700 M gal	0.06/M gal	118,100
Demineralized water	26,800 M gal	2.50/M gal	67,000
Electricity	74,492,000 kwh	0.029/kwh	2,160,300
Maintenance, 4% of direct investment			1,147,000
Analyses	9,960 man-hr	17.00/man-hr	169,300
Total conversion costs			4,796,100
Total direct costs			6,710,700
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6% of total depreciable investment			3,242,700
Average cost of capital and taxes at 8.6% of total capital investment			4,749,800
Overhead			
Plant, 50% of conversion costs less utilities			908,200
Administrative, 10% of operating labor			50,000
Marketing, 10% of sales revenue			158,900
Total indirect costs			9,109,600
Gross annual revenue requirements			15,820,300
Byproduct Sales Revenue			
Sulfur	35,300 long tons	-45.00/long ton	(1,588,500)
Total byproduct sales revenue			
Total annual revenue requirements			14,231,800

	Dollars/ton coal burned	Mills/kwh	Cents/million Btu heat input
Equivalent unit revenue requirement	9.49	4.07	45.2

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a. Basis:
New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up).
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned: 1,500,100 tons/yr, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Total capital investment, $55,180,000; total depreciable investment, $54,045,000; Total direct investment, $28,693,000.
Investment and revenue requirements for disposal of flyash excluded.
90% SO_2 removal.

Suitability for Industrial Application - Factors affecting the retrofitability, decoupling ability, and by-product utilization for industrial application should be similar to those for utility application. The process should be suitable for modularization. Because of the complexity of the regeneration system, the process may not be suitable for small boiler applications, except in locations where several scrubber modules on small boilers can be used with a central regeneration system.

Flexibility to Provide Alternate Products - Since the SO_2 collected from the flue gas is reduced to H_2S in the regeneration operation, elemental sulfur, rather than sulfuric acid, is produced as a by-product.

Regional/Site Considerations - There appear to be no regional factors that would seriously limit applicability. Supplies of petroleum coke may not be readily available in some areas, but the use of coal as a reductant might eliminate this constraint.

PROCESS ALTERNATIVES

Process alternatives (choice of carbonation process and reducing agent) are being investigated by the developer. More information is required about the process before significant alternatives can be suggested.

SUMMARY

The major advantage of the Aqueous Carbonate Process is its ability to produce sulfur with a solid carbonaceous reducing agent, eliminating the need for a reducing gas that must be produced from natural gas or by coal gasification. The decoupled nature of the process makes the gas-cleaning subsystem the sole operational interface with the flue gas source, and allows regeneration to be carried out at a distance from the scrubber. The need for reheat has been eliminated in many applications by scrubbing with a spray dryer scrubber with amounts of scrubbing liquid too low to saturate the flue gas. Although the individual process steps have been demonstrated at the pilot plant level, integration of process components has not yet been demonstrated at any level of development. A key to the success of the ACP is the successful operation of the molten salt reduction step which produces a very corrosive melt. Other potential problem areas of the process include the quench and solids filtration steps. Limited supplies of petroleum coke will make the use of coal as a reductant more attractive. The coal may, however, intensify problems with contaminants in the regeneration subsystem. Successful operation of the AI carbonation process is also important to the success of the ACP, since other carbonation processes have significantly higher energy requirements. The major area for further research is the integration of process sections. Further research is also needed in the use of coal as a reductant, and additional data on process operation would be helpful in designing a 100 Mw module.

References - BO-103, GE-101, OT-R-051, RO-158, SL-064

BERGBAU-FORSHUNG/FOSTER WHEELER DRY ADSORPTION PROCESS

The Bergbau-Forschung/Foster Wheeler process uses the concept of dry carbon adsorption of SO_2 and thermal regeneration of the carbon. A flow diagram for the process is presented in Figure 1. Flue gas from the boiler passes through dust collection equipment to remove the bulk of the particulate matter. The gas enters the absorber at temperatures between 250-300°F. The flue gas passes through one or two beds of activated char where SO_2, SO_3, oxygen, and water vapor are adsorbed on the char. The following reactions take place in the presence of activated char:

$$SO_{2\,(g)} + \tfrac{1}{2}O_{2\,(g)} \xrightarrow{\text{char}} SO_{3\,(g)}$$

$$SO_{3\,(g)} + H_2O_{(g)} \xrightarrow{\text{char}} H_2SO_{4\,(\ell)}$$

The sulfuric acid formed remains in the pores of the char. The spent char is conveyed to a regeneration vessel where the char is mixed with hot sand at a mixture temperature of about 1200°F. The following reactions take place in the regeneration step.

$$H_2SO_{4\,(\ell)} \rightarrow H_2SO_{4\,(g)}$$

$$H_2SO_{4\,(g)} \xrightarrow{1200°F} H_2O_{(g)} + SO_{3\,(g)}$$

$$2SO_3 + C_{(s)} \xrightarrow{1200°F} CO_{2\,(g)} + 2SO_{2\,(g)}$$

The carbon in the third reaction is supplied by consuming part of the char absorbent. The char is recycled to the adsorber and the sand is recycled to a sand heater where it is reheated to about 1500°F.

The off gas from the regenerator contains about 20 volume percent SO_2 and can be used to make sulfuric acid or sulfur. If the SO_2 were to be used to make sulfuric acid the gas would first be cooled and cleaned before being sent to the acid plant. If sulfur were to be produced the gas could be sent to the Foster Wheeler proprietary RESOX process. The gas would then be taken directly from the regenerator and reacted with crushed anthracite coal at 1100-1500°F to form elemental sulfur. Foster Wheeler generally includes the RESOX process in its Bergbau-Forschung/Foster Wheeler system designs.

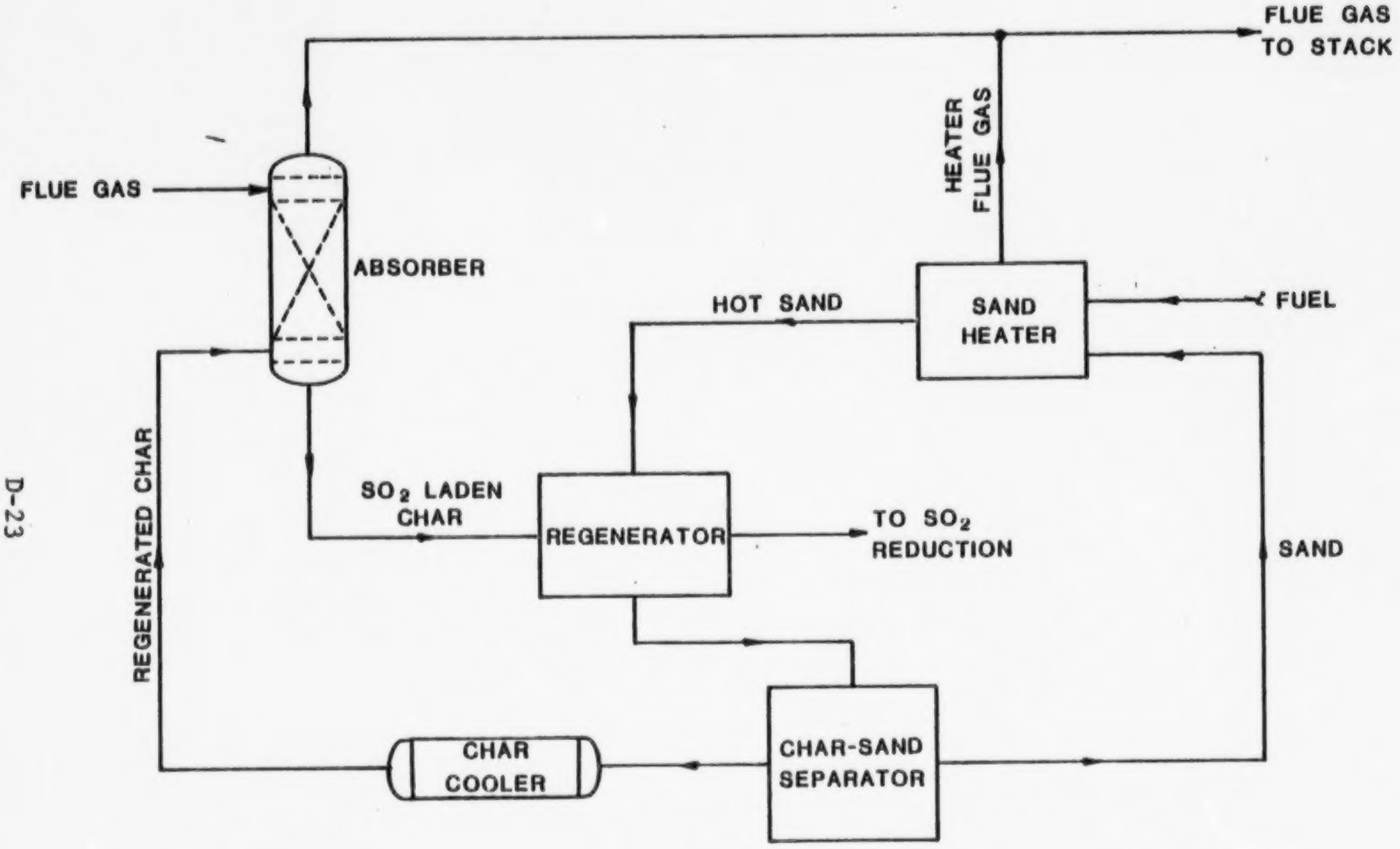
FLUE GAS
ABSORBER
REGENERATED CHAR
SO_2 LADEN CHAR
REGENERATOR
TO SO_2 REDUCTION
HOT SAND
SAND HEATER
HEATER FLUE GAS
FLUE GAS TO STACK
FUEL
SAND
CHAR-SAND SEPARATOR
CHAR COOLER

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR BERGBAU-FORSCHUNG PROCESS

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - The process has shown the capability of removing up to 97 percent of the inlet SO_2 in pilot plant testing. FW reports that the EPA views the sand heater as a process heater that does not require SO_2 controls, but some state regulations will require the sand heater flue gas be sent to the absorber for SO_2 removal.

Multipollutant Control - An initial particulate collection device precedes the BF/FW absorber. In pilot plant testing by BF, the particulate removal efficiency was 93 to 96 percent when the inlet dust loading ranged from 0.2 gr/scf to 1.3 gr/scf. Fine particulate removal was also demonstrated in one test when 67 percent of the fines were removed at an inlet dust loading of 0.061 gr/scf. The potential of the adsorber to act as the primary particulate control device has not been determined.

A reduction of NO_x was recorded at the BF pilot plant at Welhiem, West Germany, but was not adequately substantiated. FW reports that NO_x removal varying from 10 to 40 percent was demonstrated at Scholz Station. Hydrocarbon adsorption is also predicted by FW. Any hydrocarbons captured are expected to burn off either during char regeneration or RESOX reduction. Hydrochloric acid ($HC\ell$) present in the flue gas might also be expected to absorb in water on the char. At the BF Lunen facility, a 40 percent reduction in chlorides and fluorides has been reported.

Secondary Pollution Problems; Air - Attrition of the char pellets in the adsorber to produce carbon fines that might be entrained in the cleaned gas to the stack would be very undesirable since the pores of the fines are loaded with sulfuric acid. The design of the Scholz adsorber allowed a significant carryover of fines to occur, but the Lunen adsorber gave off a very low concentration of carbon particles. The problem appears to be solvable.

Secondary Pollution Problems; Water - A purge from the char cooler water loop might be necessary if the water stream from the condenser is not completely evaporated in quenching. Soluble salts could build up in water out of the char cooler. Treatment of this purge stream may be required.

Secondary Pollution Problems; Solid - The major by-product of the BF/FW Process, other than elemental sulfur, is relatively small quantities of coal ash. Fly ash streams from the absorber, and cyclone on the sand heater flue gas, and a purge of sand and/or ash from the sand heater loop (if necessary) should be compatible with boiler fly ash and could be sent to the utility ash disposal systems. If RESOX is used, the ash stream from the RESOX unit will contain significant quantities of unburned coal and, thus, might be combusted in the boiler. If combustion is not desirable or practical, this ash could also be sent to the utility ash disposal system.

Energy Intensiveness - Material and energy balance calculations were based on the following values for operating variables:

- Half of the gas goes through one adsorber stage and the other half goes through two adsorber stages. Pressure drop for gas through one stage is 11 inches of water and for gas through two stages is 17 inches of water.
- Char consumption is 0.125 pounds per pound of SO_2 fed to the adsorber.
- No gas reheat is necessary.
- The sand heater flue gas is cycled to the adsorber. If this gas is exhausted to the stack the raw material and utility requirements will be reduced about 5 percent.
- The RESOX process is used to convert the SO_2 to sulfur. The ash from the RESOX process is not burned in the boiler to recover the heating value of the unreacted coal.

Table 1 presents the calculation results.

Most of the energy required for the process is for the sand heater and RESOX reduction unit. Some of the heating value from the RESOX unit could be recovered by burning the unreacted coal/ash product in the boiler. The overall energy requirement for the process is about average when compared to other first and second generation FGD processes.

TABLE 1. RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE BF/FW PROCESS

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (dry)

		Amount
Raw Materials		
Sand	(lb/hr)	800
Char	(lb/hr)	3,100
Utilities		
Boiler Feedwater	(10^3 gal/hr)	3
Electricity		
Adsorption	(kw)	6,400
Regeneration	(kw)	1,300
Reduction	(kw)	100
Coal		
Plant	(MM Btu/hr)	210
Anthracite	(MM Btu/hr)	160

DEVELOPMENT STATUS

Overall Status - The BF/FW Process has been thoroughly and successfully tested at the bench, pilot, and prototype level in West Germany. In 1963, research and development began using a 20 scfm bench scale system that included adsorption and regeneration steps. A process for the manufacture of char was developed concurrently in a facility which could produce approximately 5000 tons per year. As a result of the bench scale work a pilot plant operating on a 1,750 scfm slip stream of flue gas from a 35 Mw pulverized coal-fired boiler was operated from 1968-1970. A prototype 45 Mw unit was installed by BF in 1974 at the Kellerman Power Plant in Lunen, West Germany. The completely integrated process operates on an 88,000 scfm slip stream from a 350 Mw coal-fired peaking service boiler. Off-gas from the regenerator is treated in a modified Claus unit (BAMAG) to produce elemental sulfur. Testing at the prototype unit, which is sponsored by the West German government, is scheduled to end in late 1978.

The first fully integrated application of the BF/FW Process using RESOX was demonstrated by FW on a 47.5 Mw coal-fired boiler at Gulf Power's Scholz Steam Plant. The unit consisted of a 20 Mw adsorption section and a 47.5 Mw reduction section (RESOX). This was the first facility which employed a two-stage adsorber.

The facility operated intermittently from August 1975, to May 1976. The unit experienced only limited success due primarily to mechanical problems or failures caused by FW in efforts to reduce costs. The BF system at Lunen, West Germany, is the most successful system to date and is more representative of the process than the system at Scholz.

Use of Commercialized Technology - Most of the process areas have been demonstrated industrially. The materials of construction used in the system are primarily carbon steel. No exotic metals or lined equipment (other than refractory lined) is required or used in the system.

The char consumption at Lunen has ranged from 0.12 to 0.18 pounds per pound of SO_2 fed to the absorber. BF states that char makeup should be somewhere between the two values. Also, stronger char which is now available should reduce makeup requirements.

Process Controllability - Temperature control is a recurring problem in carbon adsorption due to potential problems with ignition of the char in the bed. The operation at Lunen was satisfactory in this respect, but a nitrogen purge for the adsorber must be provided for emergencies and if close operating control is required. Air leaks in the system will probably have to be located and corrected for each individual application.

The most difficult design area in the process is char regeneration. The uniform mixing of sand and char and the minimum resistance to upward flow of the evolved gases should be achieved for optimum operation. The sand heating systems at both Lunen and Scholz have performed well. The use of coal as the fuel for sand heating has not been evaluated at either installation, but would be highly desirable.

ECONOMIC AND TECHNOLOGICAL FACTORS

Independent economic analysis of the Bergbau-Forschung Process was not available. Stone and Webster has reported costs from Foster-Wheeler of $41,620,000 for equipment and materials. If this were estimated in the same manner as other costs presented in this report and adjusted to a 1979 basis through application of engineering fee, contractor fee, contingency, interest during construction, and other factors, the total capital investment figure would be approximately $80,000,000. Operating costs for the process were not estimated due to the proprietary nature of the flow sheets. The process does not appear to be subject to significant cost decrease or increase due to changing technological factors. The process has been tested fairly thoroughly at the prototype level and the technology is fairly well developed. One area that could reduce costs to a small degree is full integration of the RESOX process such that the ash/coal mixture from the RESOX could be used as absorbent char.

APPLICABILITY

Suitability for Utility Application - The BF/FW Process is limited in its retrofit potential because of the large adsorbers and solids conveying system. Also, unless extensive conveying systems are employed, it will be necessary to locate both the adsorption and regeneration sections near the stack. The sulfur or sulfuric acid production unit can be located at a position more remote from the stack.

Turndown of the adsorber to about 15 percent of full load is possible according to FW through decreasing char flow rate. Duplication of the regeneration section and RESOX process (if used) into several modules allows sufficient turndown capability to match the adsorber. The BF/FW Process also has the potential for relatively simple decoupling of process areas. Insulated storage tanks can be provided for this purpose.

The acceptability of the process to the utility industry may be a problem. The process requires sensitive control, is complicated, and uses extensive solids handling equipment which transports char at high temperatures. The long term reliability of this equipment is undetermined and may be a potential problem with the process.

The sulfur or sulfuric acid by-product should be marketable in the U.S.

Suitability for Industrial Application - The process retrofitability, decoupling ability, and by-product marketability are the same for industrial application as for utility application. Modularization of the adsorption and regeneration sections is possible. The process is more applicable to large boilers than to small boilers because of the large amount of regeneration equipment required for the process. It would not be cost effective for a small boiler application to use a complicated process requiring large amounts of equipment.

Flexibility to Provide Alternate Products - The concentrated SO_2 stream from the process can be used to make sulfur or sulfuric acid.

Regional/Site Considerations - The availability of adsorbent char in the United States is a potentially limiting factor in the application of the BF/FW Process. BF asserts that the lag time associated with construction of a utility would enable them to license their technology to U.S. companies and have production underway in time to meet the needs of the utility.

PROCESS ALTERNATIVES

The BF/FW Process has been successfully demonstrated on the prototype level. Operational problems do exist with the process, but are not considered to be unsolvable. This section describes process alternatives which could offer potential improvements to the process.

RECOAL - A prospect for process improvement and simplification is to use the spent RESOX reactant known as RECOAL as the adsorbent for SO_2 in the process. FW has done some bench-scale work on this concept. They report that as the coal moves through the RESOX reactor a pore structure is created under the reactor conditions. They claim that when the RECOAL passes through a series of adsorption and thermal regeneration cycles its ability to adsorb SO_2 increases markedly and is comparable to BF char. If RECOAL proved to be an acceptable adsorbent, the next step would be to combine the regeneration/conversion step in one RESOX reactor. The pollutant gases would be desorbed at one level in the RESOX unit and then converted to gaseous sulfur at a higher temperature region. The RECOAL out of the bottom of RESOX would then be recycled to the adsorber. It should be remembered that this step is conceptual at this point and would need a substantial amount of development before becoming commercial.

Westvaco Regeneration - Another alternative to the present type of regeneration scheme used in the BF/FW Process is to use the regeneration scheme which is employed in the Westvaco Activated Carbon Process. This would greatly reduce char losses by eliminating chemical consumption of char, but would require large amounts of hydrogen for a reducing gas. In the Westvaco Process the acid laden carbon is regenerated by reducing the acid with hydrogen in several steps. In the first step the loaded carbon is fed to a reactor where most of the acid is reduced to sulfur at 300°F by an H_2S gas stream. The carbon is then preheated to 750°F by a hydrogen stream at 1300°F which is produced by some type of hydrogen production process. The hydrogen stream is reheated and sent to a reactor where the carbon is regenerated by thermally stripping the sulfur from it and at the same time reacting with three-fourths of the sulfur to produce H_2S for use in the sulfur generator. The off-gas is cooled to condense out sulfur and the carbon is cooled and sent back to the adsorber.

The Westvaco regeneration scheme was developed to minimize the chemical consumption of the carbon adsorbent which occurs in the BF/FW Process. The Westvaco Process uses hydrogen to reduce the H_2SO_4 instead of carbon. By avoiding this carbon consumption, Westvaco is able to use a more expensive adsorbent with high activity toward SO_2 adsorption. However, the advantage of using hydrogen over carbon as a reductant will hinge on the price differential between hydrogen reducing gas and the activated carbon absorbent.

SUMMARY

The BF/FW Dry Adsorption Process has been fully and successfully demonstrated at the prototype level. The RESOX unit, which is not necessarily part of the process, must still be demonstrated above the pilot scale. A major disadvantage of the process is the large amount of solids handling equipment needed to move the hot char from one process section to another. The long term reliability of the solids handling equipment is still in question. Another major drawback to the process is the large amount of makeup char required due primarily to chemical consumption and secondly to attrition. Advantages of the process include no flue gas reheat requirement, chemical simplicity, potential for NO_x removal, and low makeup water requirements.

References - BI-031, BI-073, DR-050, HA-352, MU-085, OT-R-051, ST-292

CHIYODA THOROUGHBRED 121 PROCESS

The Chiyoda Thoroughbred 121 (CT-121) process is a second generation process that Chiyoda expects to replace their CT-101 process. Many of the CT-101 process steps are combined in the CT-121 process, which utilizes a single reactor system to capture SO_2, oxidize it, and neutralize the resulting sulfuric acid with limestone. A flow diagram for the process is shown in Figure 1.

Hot flue gases are cooled in a water scrubber and sparged into a tank containing water, limestone, and gypsum. Air is also sparged through the solution to oxidize calcium sulfite to calcium sulfate. The flue gas is routed through mist eliminators, reheated, and discharged through the stack. Gypsum is continually removed from the bottom of the scrubber as a slurry and pumped to centrifuges. The resulting gypsum stream can be landfilled or sold for wallboard production. The liquid stream from the centrifuge is mixed with limestone and recycled to the scrubber, closing the water loop and adding makeup limestone.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - The CT-121 process should remove 90 percent of entering SO_2. Higher SO_2 removal could be obtained at the cost of higher pressure drops and capital costs. It would be necessary to increase contact time in larger scrubbers with more severe breakdown of bubbles by increased sparger pressure drop.

Multipollutant Control - The CT-121 process does not appear to offer potential for multipollutant removal.

Secondary Pollution Problems; Air - Secondary air pollution problems appear to be limited to mist from the absorber. This should not present serious problems.

Secondary Pollution Problems; Water - Disposal of gypsum as landfill could cause some groundwater pollution. Gypsum is known, however, to be a stable landfill material and these problems should be minimal.

Secondary Air Pollution Problems; Solid - Solid pollution problems appear limited to gypsum that must be landfilled if a suitable market is not available. This is generally regarded as a stable material and problems should not be serious. Other industries use the stacker method to dispose of gypsum in stacks and this should be applicable here. Testing of this method is required to verify this, however.

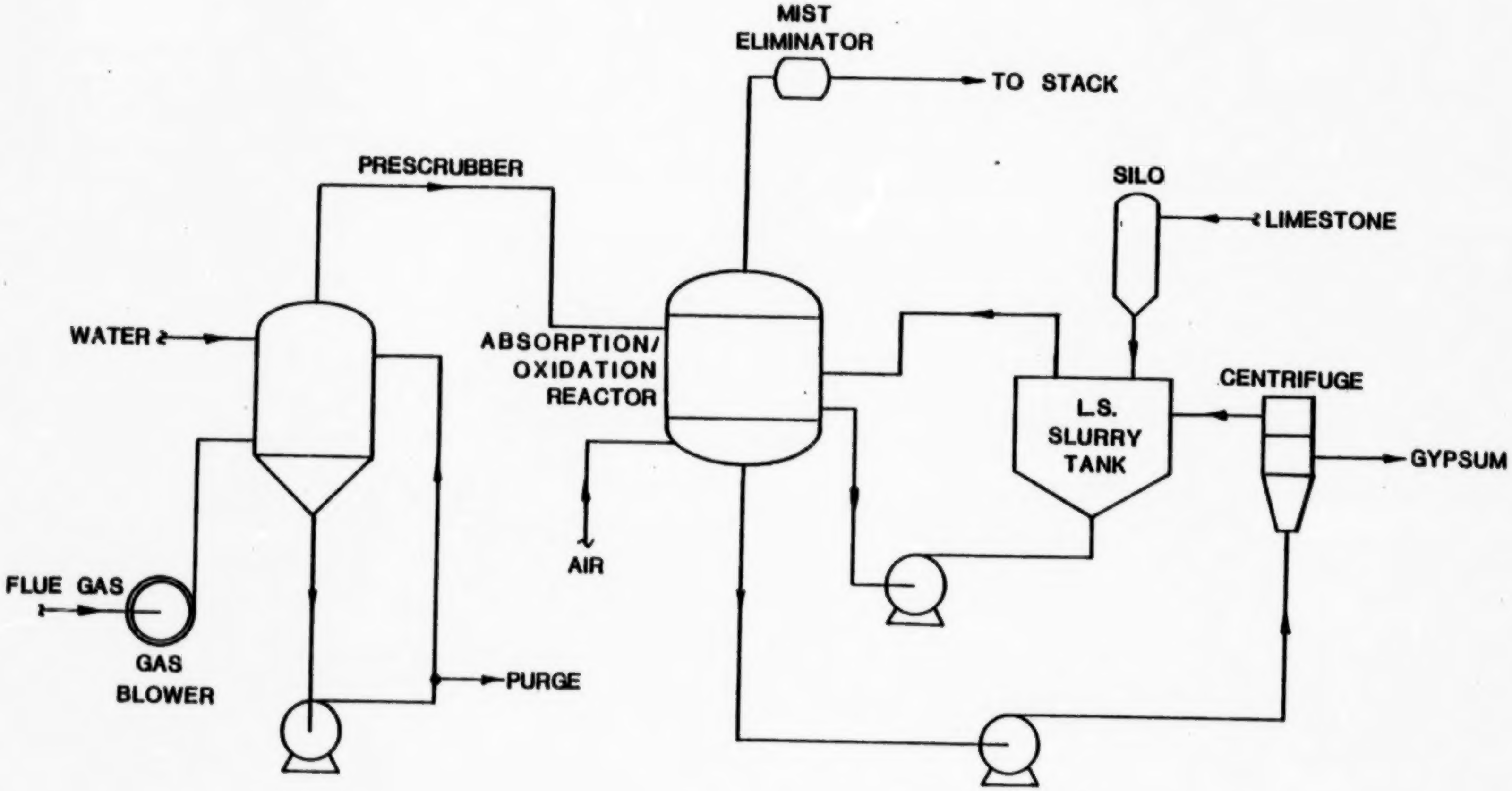
MIST
ELIMINATOR
TO STACK
PRESCRUBBER
SILO
LIMESTONE
WATER
ABSORPTION/
OXIDATION
REACTOR
CENTRIFUGE
L.S.
SLURRY
TANK
GYPSUM
AIR
FLUE GAS
GAS
BLOWER
PURGE

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR CHIYODA THOROUGHBRED 121 PROCESS

Energy Intensiveness - The process was developed in order to reduce the energy costs and capital costs of the CT-101 Process. The process should have relatively low energy requirements compared to water scrubbing as used by the CT-101 Process, with energy usage concentrated in the fans to provide pressure drop for the sparger and the liquid head in the scrubber, the pumps for movement of gypsum slurry and limestone makeup and the centrifuges required to dewater the gypsum. Reheat of the stack gas is also required. Raw materials for the process are limestone and water. It appears that the reaction can be made to occur with virtually stoichiometric amounts of limestone. Currently, the process is at too early a stage of development to quantify raw material requirements with great accuracy, but a rough approximation is presented in Table 1. These numbers are not designed to provide exact requirements, but rather to present the order of magnitude of such requirements.

TABLE 1. RAW MATERIAL AND UTILITY REQUIREMENTS FOR THE CT-121 PROCESS

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (dry)

Raw Materials		
Limestone	tons/hr	20
Water	M gal/hr	104
Utilities		
Electricity	kw	12,000
Reheat Steam	MM Btu/hr	48.6

DEVELOPMENT STATUS

Overall Status - Development of the CT-121 Process was initiated in 1975 in an effort to reduce the cost and complexity of the commercial CT-101 Process. Tests were initiated at the bench and laboratory scale and finally at the 750 scfm level. A conceptual design of a 125,000 scfm plant has been completed and plans are now under way to convert the 23 Mw CT-101 plant at Southern Company's Scholz Power Station to a CT-121 Process configuration for further testing.

Use of Commercial Technology - The mechanical and structural components of the CT-121 are used in other services at this time. The process chemistry has not been demonstrated on a large scale and this step is now underway.

Process Controllability - Control of the CT-121 process can be accomplished by monitoring pH levels in the absorber. The process should be rather easily controlled and rather insensitive to process upsets. However, ability of the process to follow load could be limited by sparger performance. As gas velocity through the sparger decreases, pressure drop decreases and bubble size increases as a result. This decreases mass transfer and SO_2 removal. It may be necessary to use multiple absorbers or a manifold system to distribute gas into any of a number of spargers in the absorber. The processing techniques utilized should be fairly acceptable to the industry although they could present some problems in the areas of scrubber operation.

ECONOMIC AND TECHNOLOGICAL FACTORS

The CT-121 process is at too early a stage of development at this time to allow accurate economic assessment. However, the process appears to offer potential for cost advantages. The process developer reports the process to have capital and operating costs on the order of 50-60 percent of the already commercial CT-101 process. These savings are a result of combining the absorption, forced oxidation, and neutralization vessels into a single vessel. This reduces capital costs by eliminating these vessels and operating costs by significantly reducing required liquid pumping. Total costs projected by Chiyoda for the CT-121 process indicate costs in the 3-5 mill/kwh range.

The costs of the process do not appear to be sensitive to technological factors due to the use of fairly standard and readily available equipment. However, as noted above, costs at this time are very tentative due to the undeveloped status of the process. The process does seem to have potential for some cost advantages over other FGD processes.

APPLICABILITY

Suitability for Utility Application - The Chiyoda Thoroughbred 121 process appears to be fairly applicable to the utility industry. Retrofit of the process is limited by available area. However, only the prescrubber and scrubber would need to be added in the area of the stack with the centrifugation and limestone slurrying potentially removed to a less crowded area. Marketability of the gypsum by-product would be extremely dependent upon local requirements for wallboard and, in general, it is expected that the by-product would have to be landfilled. The process could potentially be decoupled, with the use of storage ponds for the slurry during centrifuge down time. This would disrupt normal process operations and increase land requirements. Ability of the process to follow load may be limited as discussed under process controllability. Due to its relative mechanical and chemical simplicity, the process should be fairly acceptable to the utility industry.

Suitability for Industrial Application - Retrofit of the CT-121 process in industrial applications is limited by space required for the scrubber, and by landfill areas required for product gypsum disposal. If the gypsum can be sold as wallboard, this problem could be avoided. The absorption and centrifugation steps could be separated through the use of an intermediate pond. Although the process could be modularized in the absorption section, the capital requirements would be increased. The centrifugation section would probably be modularized in all applications.

Flexibility to Produce Alternate Products - The CT-121 process produces gypsum and cannot produce either sulfur or sulfuric acid.

Regional/Site Considerations - The process would seem to be most applicable in those areas where the gypsum product can be marketed. It is not, however, limited to such areas because the gypsum can be disposed of as landfill without seriously damaging process economics.

PROCESS ALTERNATIVES

Sludge Ponding - In a location where gypsum must be landfilled, it would seem that a viable alternative to centrifugation is dewatering by clarification in a pond. The overflow from the pond could be returned to the system and the gypsum could remain in the pond. A stacker system could then be used to remove gypsum from the pond to a gypsum stack. This would eliminate the need for centrifuges and subsequent gypsum transfer to landfill areas. It would also permit decoupling of the absorption section and increase system flexibility.

SUMMARY

The Chiyoda-Thoroughbred 121 process is a developing process that seems attractive for several reasons. Operation of the system should be relatively simple; capital costs and operating costs are potentially low. The process uses a plentiful raw material and produces a product that can be sold or landfilled. It is, however, undeveloped and there are many uncertainties as to its overall viability and costs. Demonstration of the plant on a large scale could resolve many of these uncertainties.

References - CH-398

CITRATE/PHOSPHATE BUFFERED ABSORPTION PROCESS

The Citrate and Phosphate (Aquaclaus) Buffered Absorption Processes are being considered together because of their similarity in concept, design, and operation. They use a buffered aqueous solution to absorb SO_2 which is subsequently converted to sulfur by reaction with H_2S. A flow diagram is presented in Figure 1.

Flue gas is quenched and prescrubbed with water to remove HCl, SO_3, and residual fly ash. SO_2 is removed by a buffered aqueous solution in an impingement tray or packed bed absorber. The flue gas is reheated to 175°F for discharge to the atmosphere. The primary reactions occurring in the absorber are as follows:

$$SO_2 + H_2O \rightarrow HSO_3^- + H^+ \qquad (1)$$

$$HCit^= \text{ or } HPO_4^= + H^+ \rightarrow H_2Cit^- \text{ or } H_2PO_4^- \qquad (2)$$

The citrate or phosphate acts as a buffer maintaining a pH of 3-5 throughout the system. The regeneration reaction requires a pH in this range.

Absorber liquor is reacted with H_2S in a series of reactors to form elemental sulfur by the following overall reaction:

$$SO_{2(\ell)} + 2H_2S \rightarrow 3S + 2H_2O \qquad (3)$$

The sulfur is concentrated and separated from the regenerated liquor. H_2S for the regeneration reactors can be produced by reacting reducing gas with two-thirds of the product sulfur from the process.

Some sulfite oxidation occurs and results in the formation of sodium sulfate which must be removed from the system by crystallization as Glaubers salt ($Na_2SO_4 \cdot 10H_2O$). The amount of sulfite oxidation in the systems has been reported to vary from one to four percent. The low oxidation rates are attributable to the presence of thiosulfate ions which are formed in the regeneration step.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - This process is capable of achieving high SO_2 removal. It can be designed to remove more than 99 percent of the inlet SO_2. Addition of absorber trays or packing height results in increased SO_2 removal at the cost of increased pressure drop across the scrubber.

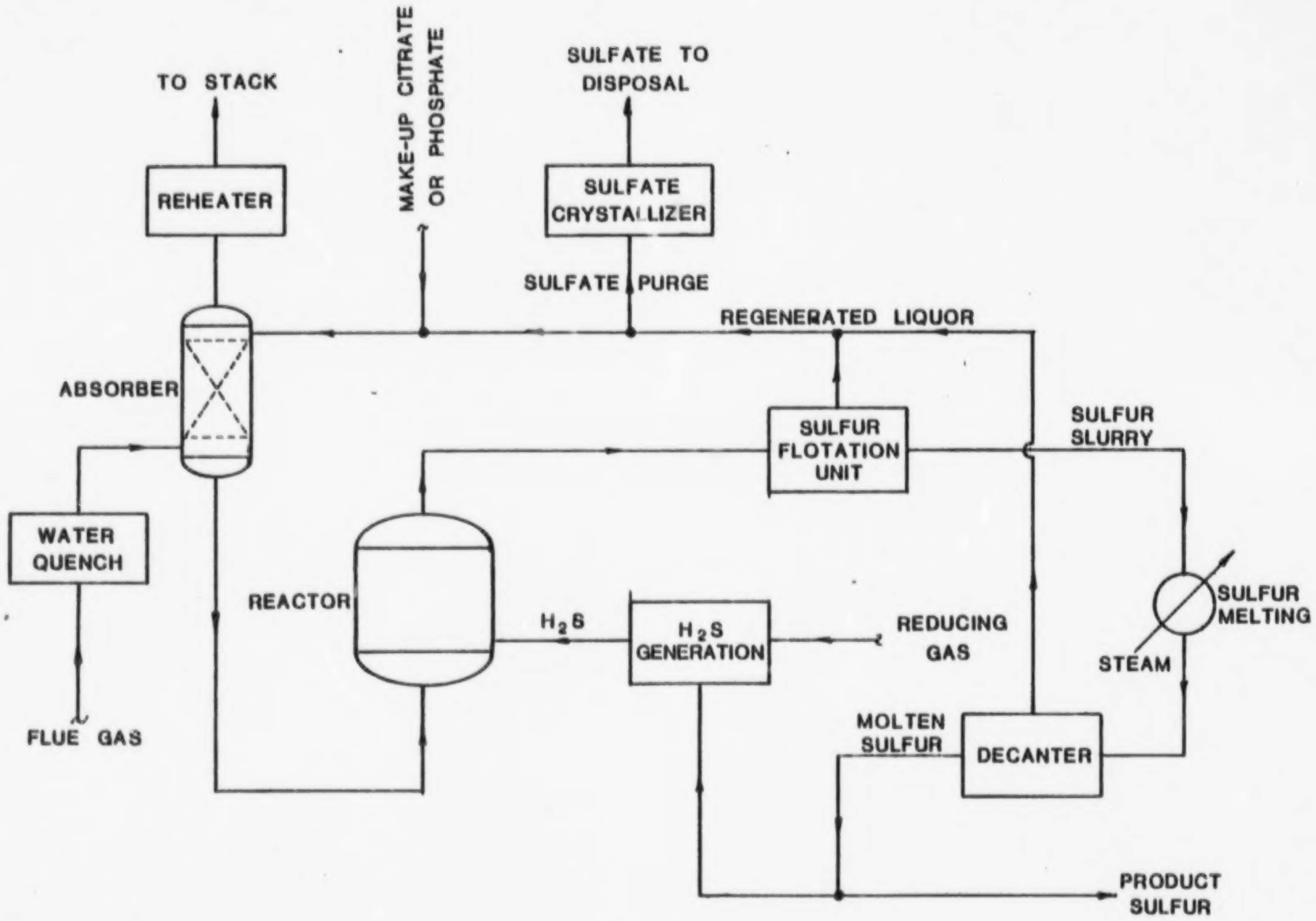
TO STACK
REHEATER
MAKE-UP CITRATE OR PHOSPHATE
SULFATE TO DISPOSAL
SULFATE CRYSTALLIZER
SULFATE PURGE
REGENERATED LIQUOR
ABSORBER
SULFUR FLOTATION UNIT
SULFUR SLURRY
WATER QUENCH
REACTOR
H_2S
H_2S GENERATION
REDUCING GAS
SULFUR MELTING
STEAM
FLUE GAS
MOLTEN SULFUR
DECANTER
PRODUCT SULFUR

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR CITRATE/PHOSPHATE PROCESS

Multipollutant Control - Particulates remaining in the flue gas out of the electrostatic precipitator should be almost totally removed in the Citrate/Phosphate Process. Some will be removed in the quench with the majority removed in the absorber. The potential for removal of NO_x by the Citrate/Phosphate Process has not yet been examined. The effect of the process on NO_x emissions is believed to be negligible.

Secondary Pollution Problems; Air - Secondary air pollution problems should be limited to fugitive emissions of H_2S. One process developer experienced hydrocarbon emissions associated with the use of kerosene in the sulfur flotation cells. Vapor recovery techniques were not employed at the pilot plant and high kerosene evaporation losses were observed. The use of air flotation cells or vapor recovery techniques can be used to solve this problem.

Secondary Pollution Problems; Water - Previous studies have expressed a concern about secondary water pollution from the Citrate Process. This concern is focused on the phosphate solution in the process and the citrate absorbing liquor. The discharge of either of these compounds is environmentally unacceptable. However, in current process configurations, those streams would be discharged only through fugitive losses. This should not present any more of a problem in the Citrate Process than in other FGD processes and would appear to be relatively easily controlled by proper plant operation and maintenance. The process has an acidic purge stream from the quench-recycle loop of about 210 GPM (500 Mw unit) which must be neutralized and pumped to the ash pond.

In summary, although there is some potential for secondary water pollution in the process, it is felt that these problems can be contained.

Secondary Pollution Problems; Solid - The major solid purge stream resulting from this process is the sodium sulfate by-product. A filter may be required between the absorber and the regeneration reactors to remove acid insoluble particulates picked up in the absorber. The sodium sulfate by-product for a 500 Mw system amounts to about 1000 lb/hr of anhydrous Na_2SO_4 based on two percent oxidation. The solids from the reactor feed filter will vary with coal composition, but are expected to be very small.

Energy Intensiveness - Major energy requirements for the process are for stack gas reheat, and reducing gas to produce H_2S for the regeneration reaction. However, for applications with a readily available H_2S stream (e.g., refineries, gasification plants) the energy requirements of the process can be significantly reduced by eliminating the reducing gas requirements. Raw material and energy requirements for the Citrate/Phosphate Process are presented in Table 1.

TABLE 1. RAW MATERIAL AND UTILITY REQUIREMENTS FOR CITRATE/PHOSPHATE SCRUBBING SYSTEMS

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (dry)

		Citrate System
Raw Materials		
Lime	(lb/hr)	1800
Citric Acid	(lb/hr)	83
Na_2CO_3*	(lb/hr)	950
Methane Reducing Gas	(10^6 Btu/hr)	192
Utilities		
Steam	(10^6 Btu/hr)	189
Process Water	(10^3 gal/hr)	50
Electricity	(kw)	10,700

*Based on an oxidation rate of 2%. Phosphate systems would have the same requirements except that phosphoric acid would be the buffer makeup and NaOH would be used instead of Na_2CO_3.

DEVELOPMENT STATUS

Overall Status - The Citrate Process was pioneered by the Bureau of Mines with developmental work also done by Arthur G. McKee, Peabody Engineering, and Pfizer, Inc. The Bureau of Mines operated a 1,000 scfm pilot unit on a lead sintering furnace tail gas for about two years. Pfizer, Peabody, McKee treated 2,000 scfm from a coal-fired industrial boiler for about seven months in 1974. A Bureau of Mines/EPA co-funded demonstration unit on 120,000 scfm of flue gas from a coal-fired utility boiler is scheduled to start up in late 1978. This unit is at St. Joe Minerals zinc smelter in Pennsylvania. The Phosphate Process was developed by Stauffer Chemical and is licensed to CHEMICO/

Envirotech. Stauffer/CHEMICO operated a 100 scfm pilot unit for six months in 1974. This unit was on an oil-fired industrial boiler. Stauffer/CHEMICO is currently actively marketing the process.

The primary technical hurdles that remain for the Citrate/Phosphate Process are H_2S generation with a hydrogen source other than methane, integration of an H_2S generation unit with the process, and a more complete understanding of the chemistry of the regeneration reaction. The process has been totally integrated except for producing H_2S from a coal based reducing gas. H_2S was produced from methane in the other installations. Stauffer has a process under development to produce H_2S from a coal based gas. The Bureau of Mines/EPA demonstration plant is planning to use both methane and carbon monoxide (CO) as reductants.

Use of Commercialized Technology - The process uses commercialized technology in the absorption and sulfur separation areas of the process. The regeneration and H_2S production areas, however, use technology still under development. Although the regeneration reactions have been demonstrated, efforts are still underway to optimize that portion of the process. As previously mentioned, the H_2S production area is under development and will probably not use currently commercialized technology.

Process Controllability - Overall process control is made somewhat difficult by the fact that the absorption and regeneration sections are coupled together. Major control problems will be in regulating the amount of H_2S fuel to the regeneration reactors to prevent odor problems from excess H_2S being emitted from the reactors and yet provide sufficient quantities to permit the regeneration reactions to proceed.

ECONOMIC AND TECHNOLOGICAL FACTORS

Capital investment and annualized costs are estimated in Tables 2 and 3. Capital costs for the process are estimated at $72,441,000, and unit revenue requirements of 7.08 mills/kwh are expected on a utility financing basis. The capital and operating costs of the H_2S plant have a large impact on overall process economics. There does appear to be potential for application of alternative technologies in this area. Application of this process at a location with available H_2S would reduce the overall process costs. If a gasification plant were used to produce reducing gas, capital costs would increase over those presented in Table 2, but direct operating costs would decrease.

Table 2.
Citrate Process
Total Capital Investment Analysis[a]

	Investment, $
Direct Investment	
Raw materials handling (unloading conveyor, elevator conveyor, feed storage bins pneumatic feed)	1,023,000
Feed preparation (conveyors, tanks, agitators, feeders, and pumps)	110,000
Gas humidification (venturi, scrubber recirculating tank, agitator, recirculation pump, cooler)	3,576,000
Flue gas handling (4 fans and ductwork)	5,220,000
SO_2 absorption (4 packed tower absorbers, 4 surge tanks, and centrifugal pumps)	9,505,000
Flue gas reheat (4 reheaters and soot blowers)	1,014,000
SO_2 reduction (2 reactor tanks, aging tanks, agitators, and centrifugal pumps)	876,000
Sulfur separation and recovery (flotation tanks, filter rotary drum, centrifugal pump, slurry tank, heat exchanger, settling tank, heating coil, and flash drum)	3,231,000
H_2S plant (H_2S plant for above battery limit, and H_2 plant for above battery limit)	10,000,000
Sodium sulfite removal (coolers, agitators, centrifuge, belt conveyor, surge tank, centrate tank, centrifugal pumps, glycol tank, and refrigeration)	624,000
Sulfur storage and shipping (sulfur receiving pit, steam heater sulfur pump, and sulfur storage tank)	1,094,000
Subtotal	36,273,000
Services, utilities, and miscellaneous	2,176,000
Total direct investment	38,449,000
Indirect Investment	
Engineering design, and supervision	2,096,000
Architect and engineering contractor	524,000
Construction expense	5,169,000
Contractor's fees	1,537,000
Total indirect investment	9,326,000
Contingency	9,555,000
Total fixed investment	57,330,000
Other Capital Charges	
Allowance for startup and modifications	5,733,000
Interest during construction	6,880,000
Total depreciable investment	69,943,000
Land	39,000
Working capital investment	2,459,000
Total capital investment	72,441,000

[a] Basis:
New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).
Coal properties: 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Investment requirements for disposal of fly ash excluded.
90% SO_2 removal; wet venturi particulate removal.

Table 3.
Citrate Process
Total Annual Revenue Requirements Analysis[a]

	Annual quantity	Unit cost, $	Total annual amount, $
Direct Costs			
Raw materials			
Lime	6,300 tons	41.00/ton	258,300
Soda ash	3,350 tons	90.00/ton	301,500
Citrate	290 tons	1340.00/ton	388,600
Natural gas	1,347,000 Mcf	3.50/Mcf	4,714,500
Catalyst			51,800
Total raw materials cost			5,714,700
Conversion costs			
Operating labor and supervision	67,920 man-hr	12.50/man-hr	849,000
Utilities			
Steam	1,326,000 MM Btu	2.00/MM Btu	2,652,000
Process water	350,000 M gal	.12/M gal	42,000
Electricity	75,000,000 kwh	0.029/kwh	2,175,000
Maintenance, 6% of direct investment			2,306,900
Analysis	10,600 man-hr	17.00/man-hr	180,200
Total conversion costs			8,205,100
Total direct costs			13,919,800
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6% of total depreciable investment			4,196,600
Average cost of capital and taxes at 8.6% of total capital investment			6,229,900
Overhead			
Plant, 50% of conversion costs less utilities			1,668,100
Administrative 10% of operating labor			84,900
Marketing 10% of sales revenue			146,300
Total indirect costs			12,325,800
Gross annual revenue requirement			26,245,600
Byproduct Sales Revenue			
Sulfur	32,500 long tons	-45.00/long ton	(1,462,500)
Total byproduct sales revenue			
Total annual revenue requirements			24,783,100

	Dollars/ton coal burned	Mills/kwh	Cents/million Btu heat input
Equivalent unit revenue requirement	16.52	7.08	78.7

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a. Basis:
New 500-Mw coal fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up).
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned: 1,500,100 tons/yr, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Total capital investment, $72,441,000; total depreciable investment, $69,943,000; total direct investment, $38,449,000.
Investment and revenue requirements for disposal of fly ash excluded.
90% SO_2 removal; wet venturi particulate removal.

APPLICABILITY

Suitability for Utility Application - The process should retrofit rather easily if sufficient space for the absorber is available. Other components of the system can be located away from the stack area. The ability of the process to follow load should be acceptable. However, there are potential problems in following boiler load in the H_2S production section unless storage for process decoupling is provided. The process could be decoupled through intermediate storage of the sorbent. However, its low SO_2 loading could make decoupling prohibitively expensive. The process can produce marketable sulfur as a by-product. The process may face problems with utility acceptability due to the overall complexity of the process.

Suitability for Industrial Application - In general, industrial suitability is affected by the above factors. The process does not have potential for modularization due to the difficulty in decoupling the process. However, this process is well suited for an industry with an available source of H_2S. The process does appear applicable to small boilers but may be less so than other FGD processes due to its overall complexity.

Flexibility for Alternate Products - This process lacks flexibility since it produces sulfur directly in the regeneration section.

Regional/Site Considerations - There are no apparent regional constraints for this process. Location at a site where H_2S is readily available would be advantageous.

PROCESS ALTERNATIVES

Double-loop Regeneration - A two-step or double-loop regeneration scheme may be possible since absorbed SO_2 reacts with H_2S in two-steps to form elemental sulfur. In the first step or loop the absorbed SO_2 is reacted with enough H_2S to produce intermediates such as thiosulfate and polythionates. The quantity of H_2S reacted with the liquor is controlled to minimize sulfur formation.

Most of this liquor out of the first loop regeneration section is recycled to the absorber. A slipstream from this recycle is taken through a second regeneration loop. Additional H_2S is added to convert the intermediates produced in the first loop to elemental sulfur. The liquor from the second loop is then added to the first loop recycle liquor. About 25 percent of the H_2S is used in the first loop and about 75 percent in the second loop. Since a more concentrated sulfur slurry would be produced than with single-loop regeneration, concentration of the slurry by air flotation might not be necessary and molten sulfur might be separated by heating and decanting only. Furthermore, decoupling would be enhanced since interstage tankage could be placed in the second regeneration loop which treats only a slipstream of the first loop recycle.

Buffer Alternatives - There are a number of feasible alternatives to the sodium citrate and sodium phosphate buffers. Sodium glycolate has been successfully tested by the Bureau of Mines. In the early 1950's, Union Oil successfully tested a sodium sulfosuccinate buffer (made by the reaction of bisulfite with maleic anhydride). Other potentially attractive buffers include sodium adipate, sodium phthalate, sodium oxalate, sodium sulfopropionate (made from bisulfite and acrylic acid), and aluminum sulfate. Although buffer makeup requirements for this process are small, the use of any of the above buffers should be evaluated to determine if they offer operational, cost, or availability advantages over the use of citrate or phosphate.

McKee Modification - Arthur G. McKee & Company has proposed a conceptual modification to the Citrate Process which eliminates the requirement for a reducing gas to produce H_2S used in the sorbent regeneration/sulfur precipitation step. A side stream of rich absorbent is diverted from the regeneration reactors and slurried with CaS. This slurry is discharged to a reactor/clarifier, where the CaS is precipitated by reaction with SO_2 and SO_3 as $CaSO_4/CaSO_3$, and a solution of NaHS and H_2S gas is produced. This NaHS and H_2S stream is used in the regeneration reactors. CaS is recovered by dewatering the reactor/clarifier underflow, and then reducing the $CaSO_4/CaSO_3$ mixture with coke in a rotary kiln. In addition to eliminating the reducing gas requirement from the Citrate Process, the $CaSO_4/CaSO_3$ precipitation and reduction steps prevent sulfate accumulation in the absorbent, so that no Na_2SO_4 purge is needed. Decoupling between the reductant regenerator and the regeneration reactors is also improved, because CaS and the $CaSO_3/CaSO_4$ mixture can be stockpiled for use as needed.

SUMMARY

The Citrate/Phosphate Process is a buffered aqueous absorption process which uses either a sodium citrate or sodium phosphate solution to absorb SO_2 from flue gas. The unique features of the process are the reaction of H_2S gas with absorbed SO_2 in the regeneration step, the separation of precipitated sulfur by flotation, and the external generation of H_2S from elemental sulfur and reducing gas. The major problems are the integration of H_2S generation with the process, the use of reducing gas from coal to generate H_2S, and the chemistry of the regeneration step. The process has been demonstrated at three pilot plants with the largest being 1 Mw. A demonstration plant on a 60 Mw coal-fired power plant boiler is planned. Acceptance of this process will be hampered by its reducing gas requirement and its lack of process separability. Research and development opportunities are present in the H_2S production and absorbent regeneration portions of the process - especially with regards to the double loop regeneration concept.

References - CA-327, CH-195, CH-198, CH-223, CH-252, KA-159, KE-063, KE-149, KO-150, KO-168, MC-125, MC-170, MC-171, MC-172, PE-171, RO-032, RO-115, SA-192, US-323, VA-112.

DOWA ALUMINUM SULFATE PROCESS

The Dowa aluminum sulfate process consists of four major processing areas: absorption, oxidation, neutralization, and filtration. Boiler flue gas is sent to a gas cooler, and then to a packed tower where SO_2 is absorbed by an aqueous solution of basic aluminum sulfate $[Al_2(SO_4)_3 \cdot Al_2O_3]$ according to reaction (1).

$$Al_2(SO_4)_3 \cdot Al_2O_3 + 3SO_2 \rightarrow Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 \quad (1)$$

The SO_2-rich liquor is then set to an oxidizing tower where the sulfite is oxidized to sulfate (reaction (2)).

$$Al_2(SO_4)_3 \cdot Al_2(SO_3)_3 + \tfrac{3}{2}O_2 \rightarrow 2Al_2(SO_4)_3 \quad (2)$$

Air is injected through specially designed nozzles, developing very fine air bubbles that accelerate the oxidation reaction. The major part of the oxidized solution is recycled to the absorber, but a fraction is neutralized with limestone in order to regenerate the basic aluminum sulfate and produce gypsum (reaction (3)).

$$2Al_2(SO_4)_3 + 3CaCO_3 + 6H_2O \rightarrow$$

$$Al_2(SO_4)_3 \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 3CO_2 \quad (3)$$

The gypsum is separated from the liquor in a thickener and centrifuged. The thickener overflow, filtrate, and wash water are recycled to the absorber. A simplified flow diagram for the process is presented in Figure 1.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - A unit treating tail gas from a double-contact sulfuric acid plant has achieved an SO_2 removal efficiency of 99%. Because the absorption capacity of the solution is lower at higher temperatures, an increased L/G would be needed to achieve this degree of removal from boiler flue gas, which has a higher temperature than acid plant tail gas, even after passing through a gas cooler. Removal efficiencies of 95% can be achieved with boiler flue gas with an L/G in the range of 35 to 75 gal/1000 scf.

Multipollutant Control - The process does not appear to have potential for removing NO_x or other pollutants.

Secondary Pollution Problems; Air - No secondary air pollution problems are anticipated.

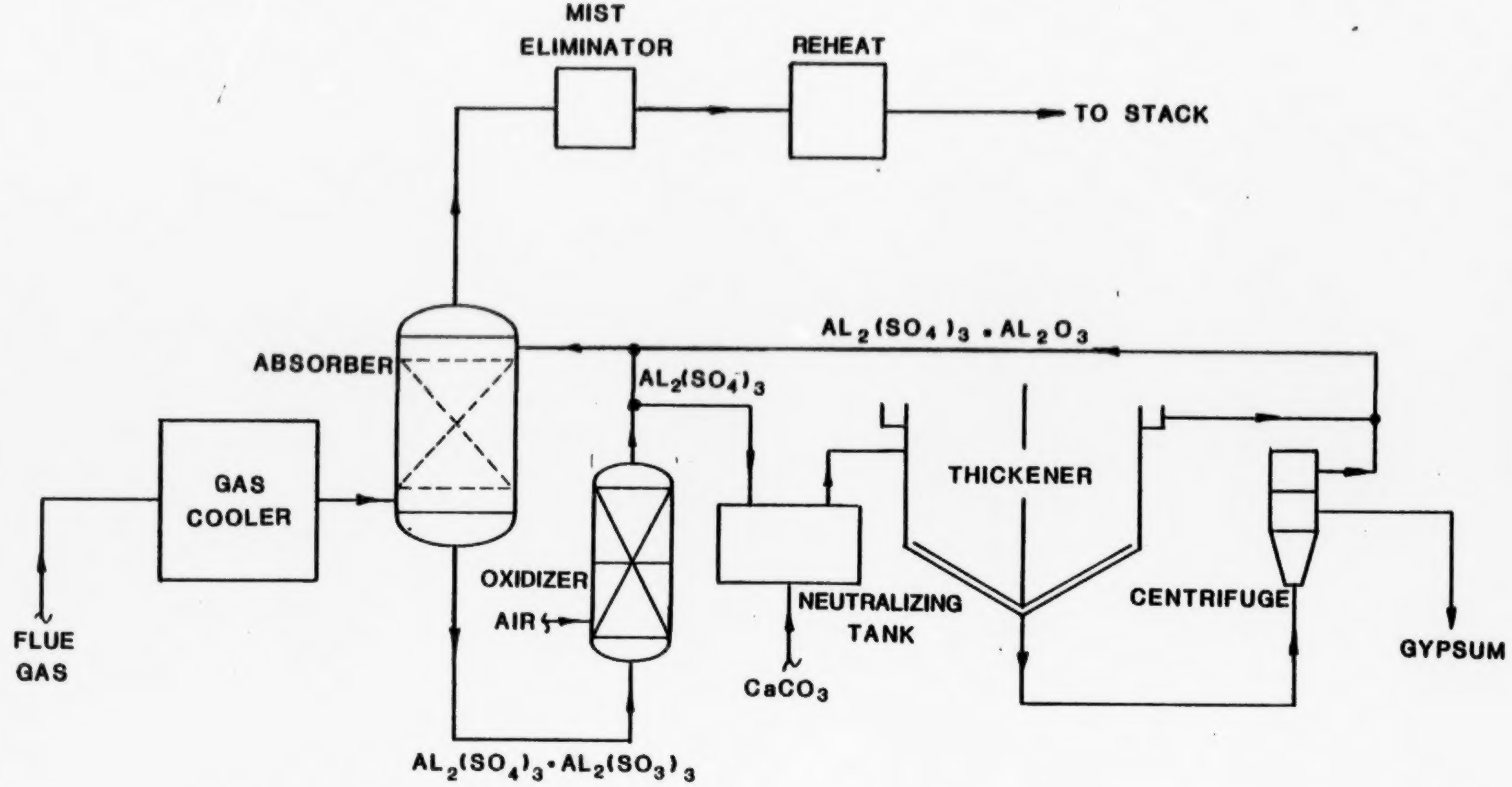
MIST ELIMINATOR
REHEAT
TO STACK
ABSORBER
GAS COOLER
FLUE GAS
$AL_2(SO_4)_3 \cdot AL_2O_3$
$AL_2(SO_4)_3$
OXIDIZER
AIR
$AL_2(SO_4)_3 \cdot AL_2(SO_3)_3$
NEUTRALIZING TANK
$CaCO_3$
THICKENER
CENTRIFUGE
GYPSUM

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR DOWA ALUMINUM SULFATE PROCESS

Secondary Pollution Problems; Water - In general, Dowa claims successful operation of the process in a closed fashion, with no liquid effluents. If marketable gypsum is to be produced, however, a small purge stream may be necessary to limit the concentration of magnesium, which may be present as an impurity in the limestone used for neutralization.

Secondary Pollution Problems; Solids - A relatively large volume of gypsum solid waste is produced. Gypsum of marketable quality can be produced, but probably could not be sold in the U.S. The gypsum produced is a more desirable waste product than the calcium sulfite/sulfate sludge produced from lime/limestone processes. Gypsum is more easily dewatered, is less thixotropic, and has a greater bearing strength than calcium sulfite. Gypsum is suitable for landfill disposal.

Energy Intensiveness - Estimates of raw material and utility requirements for the Dowa process are given in Table 1. The process has higher energy requirements than the lime/limestone or sodium double alkali processes, principally because of the energy required to compress air for oxidation of the scrubbing solution.

TABLE 1. RAW MATERIAL AND ENERGY REQUIREMENTS FOR DOWA ALUMINUM SULFATE PROCESS

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (dry)

Raw Materials		
Aluminum Sulfate, 57%	(lb/hr)	266
Limestone	(tons/hr)	19.9
Utilities		
Process and Cooling Water	(10^3 gal/hr)	42.8
Electricity	(kw)	
Gas Handling		6146
SO_2 Absorption		2655
Oxidation		1450
Slurry Processing		983
Miscellaneous*		2147
Steam†	(10^6 Btu/hr)	51.1
Solid Waste	(tons/hr)	33.4

* Includes raw material handling, feed preparation, particulate removal, solids disposal, etc.
† For flue gas reheat.

DEVELOPMENT STATUS

Overall Status - The Dowa process has been demonstrated on commercial-size units treating acid plant tail gas, metallurgical furnace waste gas, and boiler flue gas. A unit treating 2065 scfm of waste gas from molybdenum sulfide calcination (1.2 Mw equivalent) was put into operation in October, 1972. Two units treating 82,600 scfm of acid plant tail gas (47 Mw equivalent) have been in operation at Dowa Mining's Okayama plant since 1974. Two additional units, on an oil-fired utility boiler (27 Mw equivalent) and a sintering plant (17 Mw equivalent), were put into operation in 1976. These units have been fully integrated. The process has not yet been applied to a coal-fired boiler; however, negotiations are under way for a 10 Mw demonstration of the process sponsored by TVA, EPRI, and UOP/Dowa at the TVA Shawnee test site.

Use of Commercialized Technology - In general, the process uses commercially available equipment. The process technology as a whole has not been tested at a sufficiently large scale on a utility boiler to be regarded as commercial.

Process Controllability - The major process variables that must be controlled to ensure reliable operation with adequate SO_2 removal are concentration and basicity of the absorbing liquor. Basicity is defined as the degree of neutralization of aluminum sulfate solution. The higher the solution concentration of Al_2O_3 relative to $Al_2(SO_4)_3$, the higher the basicity. In general, solutions with high concentrations of aluminum, high basicity, and low temperatures have higher SO_2 absorption capacity. Solubility relationships of aluminum salts, however, are relatively complex. In commercial operation, basicity must be kept lower than 40% (pH >4 or 4.5) to prevent precipitation of aluminum from solution. This precipitation would cause plugging of the packing in the absorber. Minimum loss of aluminum in the gypsum occurs at a concentration of 15 to 20 grams/ℓ of aluminum in solution. These factors, along with SO_2 concentration of the gas and removal efficiency required, are considered in order to select the optimum concentration and basicity of the absorbing liquor.

Oxidized spent scrubbing solution is neutralized to the optimum basicity with limestone. Measurement of basicity was a problem at one of the early plants. The pH of the solution does not vary linearly with basicity. Electrical conductivity provides a good measure of basicity of the absorbent solution, but magnesium ions (which have a much higher conductivity) coming from the limestone used for neutralization gradually accumulate in the solution and interfere with the measurement.

Although magnesium ions do not disturb SO_2 absorption, they do affect gypsum crystallization. The accumulation of magnesium ions must be prevented if marketable gypsum is produced. For this reason, a small magnesium removal unit has been added to the Okayama plant. In this unit, a small part of the absorbent is neutralized with excess limestone. The aluminum in the solution is precipitated with the gypsum, but the magnesium remains in solution. The overflow from the settler is discarded to limit the concentration of magnesium ions in the absorbent. The underflow is recycled to the main neutralizing tank to avoid loss of aluminum.

Since the capacity of the solution to absorb SO_2 is lower at higher temperatures, higher L/G is required to achieve high SO_2 removal at higher temperatures. The required L/G can reportedly be decreased somewhat by adding a small amount of an inorganic catalyst to the absorbent. This catalyst promotes oxidation in the solution during absorption. A lower L/G would also be possible with flue gas from low-sulfur coal because of the increased oxidation in the absorber.

ECONOMIC AND TECHNOLOGICAL FACTORS

Estimated capital and operating costs for the Dowa Process are given in Tables 2 and 3, respectively. The capital costs for the process have been estimated at $48,217,000 and unit revenue requirements at 4.24 mills/Kwh on a utility financing basis. Capital costs for Dowa are about 5 percent lower than costs for the sodium double alkali process, due primarily to savings from disposal of gypsum without ponding. The costs for oxidation equipment in the Dowa Process are a relatively minor component of capital cost for the process (less than 5 percent of direct investment), but in any case are less than the cost for solids separation and disposal equipment for sodium double alkali.

Operating costs for Dowa are also lower than those for sodium double alkali because of the significantly lower raw material costs. Cost for electricity is a major contributor to operating costs for the Dowa Process. Electrical requirements for feed preparation, gas handling, SO_2 scrubbing, and slurry processing are higher for Dowa than for sodium double alkali. Dowa also requires additional energy to compress air for oxidation. The energy required for oxidation could possibly be decreased somewhat by the use of a catalyst to promote oxidation so that the excess air required for oxidation could be decreased. Cost for catalyst, however, would then be added to operating cost, and may offset the savings in electricity cost.

Table 2

Dowa Basic Aluminum Sulfate-Gypsum Process

Total Capital Investment Analysis[a]

	Investment, $
Direct Investment	
Material handling (silo, hoppers, feeders, conveyors, elevator, bin, dust collecting and bag filter systems)	705,000
Feed preparation (feeders, conveyor, tanks agitator, pumps, crushers, elevators, ball mills, dust collecting system, and hoist)	1,584,000
Particulate scrubbing (venturi scrubbers, sumps, tanks, agitators, pumps, soot blowers and neutralization system)	3,583,000
Sulfur dioxide absorption (TCA absorbers, sumps, tanks agitators and pumps)	6,989,000
Reheat (reheaters and soot blowers)	1,071,000
Flue gas handling (fans and ductwork)	4,722,000
Oxidation (compressors and towers)	1,088,000
Slurry processing (tanks, agitators, pumps, thickener, drum filters and conveyors)	2,878,000
Solids disposal (conveyors)	917,000
Subtotal	23,537,000
Services, utilities, and miscellaneous	1,412,000
Total direct investment	24,949,000
Indirect Investment	
Engineering design and supervision	1,831,000
Architect and engineering contractor	458,000
Construction expense	3,610,000
Contractor's fees	1,107,000
Total indirect investment	7,006,000
Contingency	6,391,000
Total fixed investment	38,346,000
Other Capital Charges	
Allowance for startup and modifications	3,835,000
Interest during construction	4,602,000
Total depreciable investment	46,783,000
Land	305,000
Working capital	1,129,000
Total capital investment	48,217,000

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a. Basis:
New 500-MW coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).
Coal properties: 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Investment requirements for disposal of fly ash excluded.
90% SO_2 removal.

Table 3

Dowa Basic Aluminum Sulfate-Gypsum Process

Total Annual Revenue Requirements Analysis[a]

	Annual quantity	Unit cost, $	Total annual amount, $
Direct Costs			
Raw materials			
Aluminum sulfate, 57%	930 tons	184.00/ton	171,100
Limestone	139,000 tons	7.00/ton	973,000
Total raw materials cost			1,144,100
Conversion costs			
Operating labor and supervision	46,500 man-hr	12.50/man-hr	581,300
Utilities			
Steam	358,000 MM Btu	2.00/MM Btu	716,000
Process water	299,880 M gal	0.12/M gal	36,000
Electricity	94,393,000 kWh	0.029/kWh	2,737,400
Maintenance, 6% of direct investment			1,496,900
Analyses	3,500 man-hr	17.00/man-hr	60,000
Total conversion costs			5,627,600
Total direct costs			6,771,700
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6% of total depreciable investment			2,807,000
Average cost of capital and taxes at 8.6% of total capital investment			4,146,700
Overhead			
Plant, 50% of conversion costs less utilities			1,069,100
Administrative, 10% of operating labor			58,100
Total indirect costs			8,080,900
Total annual revenue requirements			14,852,600

	Dollars/ton coal burned	Mills/kwh	Cents/million Btu heat input
Equivalent unit revenue requirement	9.90	4.26	47.1

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[a] Basis:
New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up).
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned: 1,500,100 tons/yr, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Total capital investment, $48,217,000; total depreciable investment, $46,783,000; total direct investment, $24,949.000.
Investment and revenue requirements for disposal of fly ash excluded.
90% SO_2 removal; wet venturi particulate removal.

APPLICABILITY

Suitability for Utility Application - The Dowa process should be applicable to utility use. Retrofits should be relatively easy, but may be slightly more difficult than for sodium/lime double alkali systems because of the higher L/G and the requirement for an oxidizer in the scrubber loop. Gypsum of marketable quality can be produced, but finding a market for it in the U.S. could be quite difficult. The scrubber should have good turndown capability. The regeneration system can be decoupled from the absorber by the use of intermediate storage. Although the oxidation tower could be decoupled from the absorber, this option would be expensive due to large storage requirements associated with the relatively high L/G requirements in the absorber. The processing techniques should be acceptable to the utility industry, but the process has not yet been demonstrated in a utility application.

Suitability for Industrial Application - Considerations affecting retrofitability, by-product utilization, and separability of process steps are similar to those for utility application. The process should be adaptable for modularization, and it has been applied successfully to a small industrial boiler.

Alternate Products - Gypsum appears to be the only feasible by-product.

Regional/Site Considerations - In general, there should be no major regional/site considerations to limit process applicability. Aluminum availability should not be a problem; however, the availability of land for gypsum disposal could limit applicability in certain areas.

PROCESS ALTERNATIVES

Organic Acid Buffers - The Dowa process uses aluminum as a buffer, with a resulting pH of about 4. Other buffers could be used with the basic Dowa flowsheet. For example, use of a nonvolatile organic acid (such as adipic acid) would allow operation at a higher pH (around 5) and, thus, at a lower L/G. Operation at the higher pH and lower L/G also allows for a simpler scrubber design. If a pH greater than 5 is maintained in the neutralization loop, lime must be used for neutralization, but an adipic acid buffer maintains a pH of around 5, low enough that limestone can still be used.

SUMMARY

The Dowa aluminum sulfate process can be operated at any level of oxidation without requiring a sulfate purge or complex operation for sulfate removal. High quality gypsum, rather than calcium sulfite sludge, is produced as a by-product, and limestone, rather than lime, is used for regeneration. The Dowa process does, however, require a higher L/G than the sodium double-alkali process because of the lower pH and absorption capacity of the scrubbing solution. The process has apparently not yet been tested on flue gas from a coal-fired boiler. Major areas for further research appear to be demonstration of the process on gas from a coal-fired boiler, and evaluation of buffers other than aluminum sulfate.

References: AN-147, AN-187, RO-190, YA-075

HÖLTER

The Hölter process has been developed in West Germany by Saarberg-Hölter. Flue gas is cleaned of particulates before being sent to the absorber, where SO_2 is absorbed in 0.5-10 weight percent clear solution of $CaCl_2$ saturated with lime. Spent scrubber solution is oxidized to produce gypsum, and slaked lime is added to replace the calcium lost in the gypsum. A special additive called "Absorben 75" (formic acid) is added to the scrubbing solution. This additive buffers the solution and thus controls pH during SO_2 sorption, prevents corrosion, increases SO_2 removal by increasing the concentration of calcium ions, and helps to prevent scaling in the scrubber. Gypsum is separated from the liquor by centrifugation. A simplified diagram is presented in Figure 1.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - The process is capable of 90 to 95 percent removal of SO_2.

Potential for Multipollutant Control - Particulates should be removed upstream of the SO_2 absorber to a level of 0.05-0.2 gr/scf. Some additional particulate removal is obtained in the absorber. These particulates are eventually removed in the gypsum by-product. Simultaneous removal of HCl and HF with SO_2 has been demonstrated at a waste products incinerator. Removal of HCl and HF achieved was 97 to 98 percent, while SO_2 removal was 87-90 percent. NO_x removal has not been reported for the process.

Secondary Pollution Problems; Air - No secondary air pollution problems are anticipated.

Secondary Pollution Problems; Water - No secondary water pollution problems are anticipated.

Secondary Pollution Problems; Solid - The process produces a by-product gypsum that has been marketed in Germany. If the gypsum cannot be sold in the U.S., it must be ponded or landfilled. Gypsum sludge is a better landfill material than calcium sulfite sludge in that it is not thixotropic and can be more easily dewatered.

Energy Intensiveness - Utility and energy requirements for the $CaCl_2$ process differ from those for conventional lime systems in several areas. The process water requirement is lower due to the lower free moisture content of the gypsum product compared to conventional waste sludge (89-90 weight percent versus 35-70 weight percent). The L/G for the Hölter system is much lower than the normal lime system so, the electricity requirements for the pumps is much smaller. The gypsum produced from the process is of a very high quality and is suitable for use as a building material. Table 1 gives a typical composition of the gypsum from the Hölter Process.

TABLE 1. TYPICAL GYPSUM COMPOSITION FOR THE SAARBERG-HÖLTER PROCESS

Component	Wt % (dry basis)
$CaSO_4.2H_2O$	94.0 - 97.0
$CaSO_3$	0.2 - 0.4
$CaCO_3$	0.1 - 0.5
Ballast material (flue dust and natural impurities in the lime)	5.7 - 2.1
	100
Gypsum Flow Rate*	38.7 tons/hr

*Gypsum by-product is assumed to contain 20 weight percent free water.

Material and energy balance calculations are presented in Table 2 and were based on the following values for operating variables:

- Rotopart scrubber with a pressure drop of 8 inches of water
- Stoichiometry - 1.02 moles CaO/mole SO_2 sorbed.
- L/G = 30-35 gal/1000 scf
- Lime composition - 95% CaO, 5% inerts.

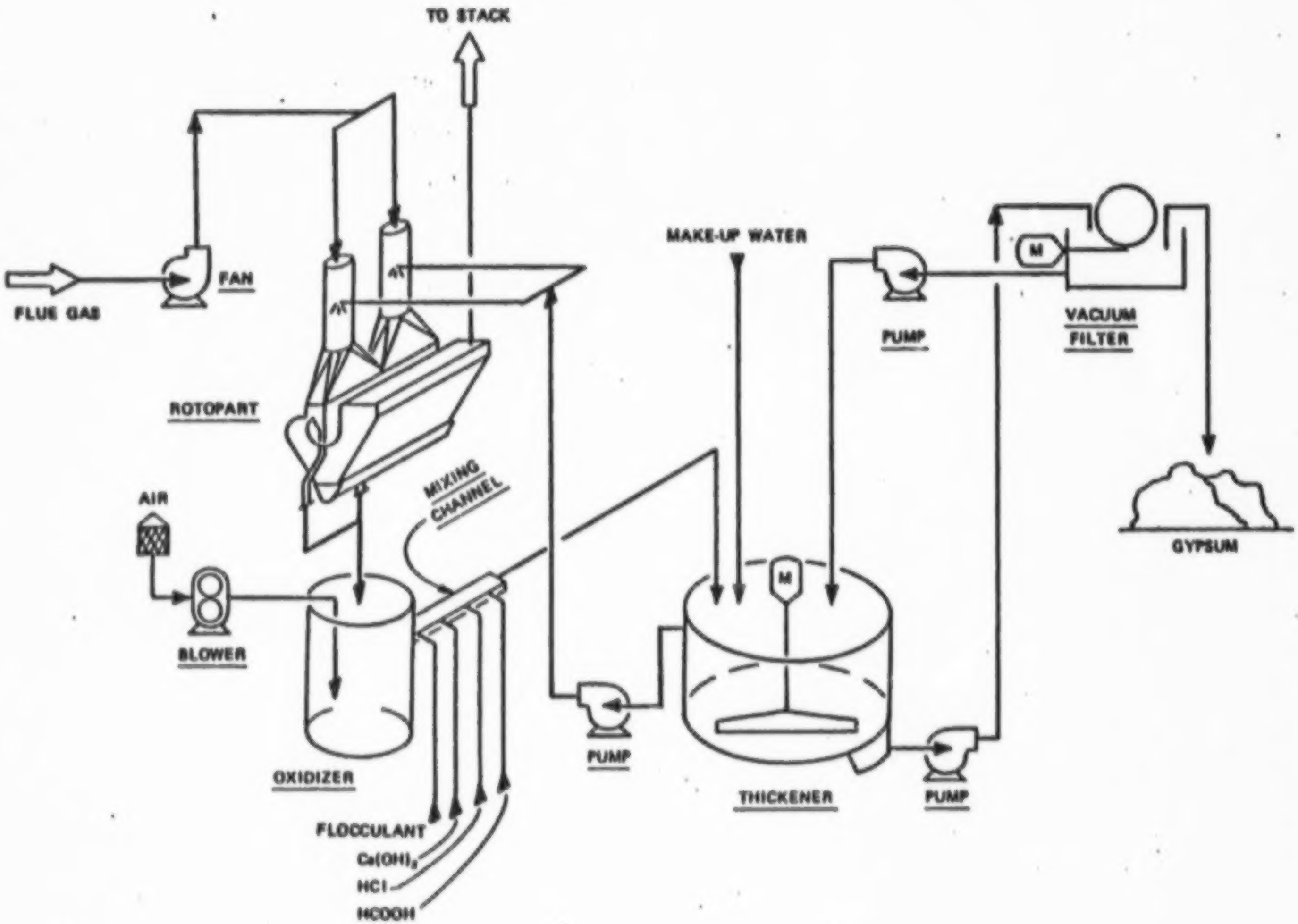
TO STACK
FLUE GAS
FAN
ROTOPART
MIXING CHANNEL
AIR
BLOWER
OXIDIZER
FLOCCULANT
$Ca(OH)_2$
HCl
HCOOH
PUMP
MAKE-UP WATER
THICKENER
PUMP
PUMP
M
M
VACUUM FILTER
GYPSUM

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR SAARBERG-HÖLTER PROCESS

TABLE 2. RAW MATERIAL AND UTILITY REQUIREMENTS FOR A HÖLTER SCRUBBING SYSTEM

Raw Materials		
Lime	(tons/hr)	11.5
Formic Acid	(lb/hr)	21.0
Utilities		
Process Water	(10^3 gal/hr)	13.2
Electricity		
Pumps and Oxidation Air	(kw)	4660
Fan	(kw)	2700
Steam (500 psig)	(10^6 Btu/hr)	48.4
Gypsum by-product*	(tons/hr)	40.7

*Gypsum by-product is assumed to contain 20 weight percent free water.

DEVELOPMENT STATUS

Overall Status - In West Germany, a small 1770 scfm pilot plant was first tested in 1973. The pilot unit showed good results, and a 40 MW prototype plant treating gas from a coal-fired boiler was constructed and started up in October 1974. This plant, which is still operating, is fully integrated using commercially available technology. Another 10 MW equivalent plant has been operating at a waste products incinerator to simultaneously remove HCl, HF, and SO_2.

In the West German installations, it is reported that there have been no problems with erosion, corrosion, or scaling and plugging. There have been no unusual mechanical problems, and the prototype plant has been operating with an availability of over 90 percent. The carbon steel scrubbing system is plastic- or rubber-lined in areas which come into contact with the gas and liquid. The I.D. fan for the scrubbing system is rubber-lined.

The West German process developers claim to avoid gypsum scaling in their process. Over 20,000 hours of scale free operation has been obtained to date on the 40 MW plant. Actual plant operating data should be examined to substantiate the claim that the system operates without gypsum scale.

Use of Commercialized Technology - In general, the process uses commercially available technology. However, the Hölter Process uses a patented rotating venturi scrubber (ROTOPART) for SO_2 absorption and mist elimination.

Process Controllability - The process is not complex. The most critical control operating parameter for the system is the pH of the scrubbing liquor. Inadequate control of this parameter can cause scaling in the system; however, use of the additive "Absorben 75" facilitates pH control.

ECONOMIC AND TECHNOLOGICAL FACTORS

Sufficient process information was not available to permit comparative process economic calculations to be performed. Since this process is similar in nature to the lime/limestone process, process economics should also be similar. However, there are several process differences which have been discussed and which are mentioned below that will affect the costs of this system in comparison to the costs presented for a limestone scrubbing system. These process differences and their expected economic effects are as follows:

- The Hölter system uses lime instead of limestone which will increase the relative operating costs, but will probably decrease capital costs.
- An oxidizer is used to produce gypsum which will increase both operating and capital costs. Electricity requirements for operating the oxidation blower have been shown to be a significant portion of the overall process electrical requirements (DOWA Process). Cost savings resulting from the increased ease of disposal of gypsum over calcium sulfite sludge may, however, partially offset the costs of oxidation.
- Operating costs should be less than lime/limestone because of low L/G rates and the lower make-up water requirement. Maintenance costs should be reduced by use of a clean scrubbing solution instead of the 5-15% slurry typical of other lime systems.

- Material costs may be higher for the process due to the large quantities of chlorides circulating in the system.

APPLICABILITY

Suitability for Utility Application - The process is well-suited for retrofit and has good turndown ability. Land is required for the absorber at the stack with the regeneration section located at some distance from the stack. It is reported that the FGD system can handle 40 to 120 percent of the design flue gas volume. Decoupling of process steps is possible through provision of intermediate solution storage. The process units should be fairly easy to operate and maintain. Waste disposal is not a problem in West Germany because the gypsum by-product is salable as wallboard, but it would probably be landfilled in the U.S. Particulates should be removed upstream of the SO_2 absorber to a level of 0.05-0.2 gr/scf. Particulates entering the SO_2 absorber are eventually removed in the gypsum by-product. The gypsum would be more suitable for ponding or landfilling than unoxidized sludge because the sulfate crystals are denser and settle better than sulfite crystals. The process should be as acceptable to the utility industry as other throwaway processes.

Suitability for Industrial Application - Industrial retrofitability, by-product utilization, and decoupling should be similar to that described for utility applications above. There are no parts of the process that cannot be modularized. The process should work very well for small boiler applications. A demonstration plant in West Germany cleaning gas from a waste products incinerator has performed satisfactorily. Besides simultaneous removal of HCl, HF, and SO_2, the system cleaned the gas entering at 482-518°F. The system was able to handle large increases in SO_2 concentration in the flue gas from 1500-3760 ppm in 2 to 5 minutes.

Flexibility to Provide Alternate Products - The process cannot reasonably produce a by-product other than gypsum.

Regional/Site Considerations - It appears that the process can be applied in any region in the country since limestone, which is used to make lime, can be found in all parts of the U.S.

PROCESS ALTERNATIVES

Limestone Use - The use of limestone instead of lime as the SO_2 absorbent may be beneficial because limestone is less expensive than lime. Economic trade-offs between operating cost savings and capital cost increase would need to be examined. The developers of the Hölter Process report that limestone can be used in their process, but lime has been used in all the installations of the process to date. Therefore, the use of limestone in the process should be further investigated to develop operating parameters and comparative economics.

SUMMARY

The Hölter scrubbing process has been demonstrated on the prototype level (40 MW) in West Germany. The disadvantages of the process are the use of lime instead of limestone, a possible chloride makeup requirement, and the possibility of gypsum scaling. The process developers claim that gypsum scaling is not encountered in the process, but this should be substantiated by examining actual plant operating data. The advantages of the process are low L/G and a low overall energy requirement. Initial RD&D efforts should be focused upon developing reliable costs for this process. If process economics show advantages over competing throwaway systems, then construction of a demonstration unit in the United States may be warranted.

References - AN-147, BE-466, ES-029.

INTEGRATED CAT-OX PROCESS

The Integrated Cat-Ox process uses catalytic oxidation of SO_2 to SO_3 and subsequent absorption of SO_3 in a sulfuric acid stream to produce a 75-80 percent sulfuric acid product. The three main sections of the process are hot electrostatic precipitation, catalytic conversion, and absorption. A flow diagram is presented in Figure 1.

Flue gas from the boiler is routed through hot electrostatic precipitators (ESP) to reduce particulate loading to 0.005 gr/scf or less. Operation of the ESP at temperatures of 850°-900°F which are required for subsequent catalytic conversion is some 400°-500°F above the normal temperature for ESP operation.

Flue gas is then passed across a bed of vanadium pentoxide catalyst where SO_2 is converted to SO_3 with an ultimate conversion of 95-99 percent. The converted flue gas is routed through the power plant economizer and air preheater sections.

The final section of the Integrated Cat-Ox process is the absorption section. Flue gas is countercurrently contacted with a 75-80% sulfuric acid solution and the majority of the SO_3 and some of the water in the flue gas are condensed into the liquid stream. The absorber can operate at 250°F due to the low vapor pressure of sulfuric acid and consequently it is not necessary to reheat the flue gas for discharge to the atmosphere. The hot acid from the absorber is cooled and returned to the absorber. A side stream is withdrawn, cooled, and sent to sulfuric acid product storage.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - The process generally removes 93-95 percent of the flue gas SO_2. Modification can increase efficiency to 99 percent by increasing the size of the catalyst bed and going to a two stage absorber design.

Multipollutant Control - Only some trace elements, halogens and SO_3 that were originally in the flue gas can be credited to the process as multipollutant removal. However, due to low particulate levels necessary for catalytic conversion, the process results in lower particulate levels than are generally emitted. No NO_x control is anticipated.

Secondary Pollution Problems; Air - Acid mist from the absorber can be controlled to levels lower than current standards and should not present problems. It will be necessary to bypass the catalyst bed during absorber outages due to the increased public health problems with SO_3 as opposed to SO_2.

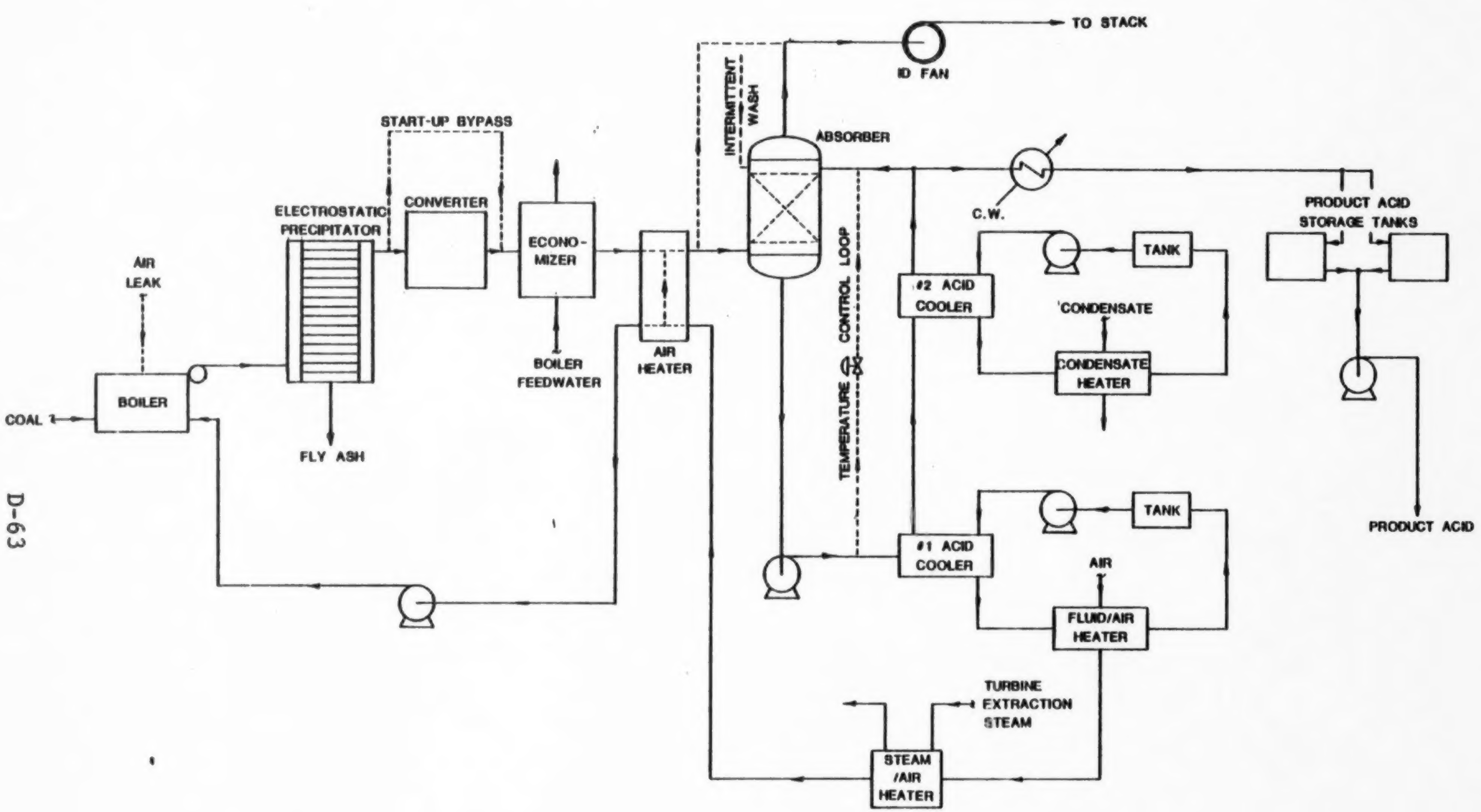
TO STACK
ID FAN
INTERMITTENT WASH
START-UP BYPASS
ABSORBER
C.W.
PRODUCT ACID STORAGE TANKS
ELECTROSTATIC PRECIPITATOR
CONVERTER
ECONO-MIZER
AIR LEAK
TANK
#2 ACID COOLER
CONDENSATE
CONDENSATE HEATER
TEMPERATURE CONTROL LOOP
BOILER
COAL
AIR HEATER
BOILER FEEDWATER
FLY ASH
TANK
PRODUCT ACID
#1 ACID COOLER
AIR
FLUID/AIR HEATER
TURBINE EXTRACTION STEAM
STEAM /AIR HEATER

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR INTEGRATED CAT-OX PROCESS

oz-1836-2

Secondary Pollution Problems; Water - Fugitive emissions from acid pumps could cause water pollution. This should not be a serious problem.

Secondary Pollution Problems; Solid - There will be a requirement to dispose of vanadium pentoxide catalyst. However, this problem has been solved in other industries and should not be significant.

Energy Intensiveness - Integrated Cat-Ox is a low energy consumption process. Stack gas reheat is not required. Liquid/gas ratios in the absorber are not large. Reducing gas is not required. The exothermic reactions of SO_2 to SO_3, sulfuric acid formation, water condensation and acid water mixing actually provide additional energy to the boiler system that is recovered in the acid coolers. This heat would not be recovered in a conventional power plant and thus, represents a contribution to the overall plant efficiency. Process raw material and energy requirements are summarized in Table 1.

TABLE 1. RAW MATERIAL AND UTILITY REQUIREMENTS FOR INTEGRATED CAT-OX SCRUBBING SYSTEM

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (dry)

Raw Materials		
Catalyst	liters/yr	113,100
Utilities		
Steam	M lb/hr	27
Heat Credit	MM Btu/hr	(141)
Process Water	m gal/hr	44.6
Electricity	kw	13,030

DEVELOPMENT STATUS

Overall Development - Two installations of the Cat-Ox process have been built to date: a 15 Mw pilot plant at Metropolitan Edison (1967-1969) and a 110 Mw demonstration plant at Illinois Power's Wood River Plant in 1973. The smaller plant was operated as an integrated system but the Wood River Plant was based upon the reheat Cat-Ox process which is used in retrofit applications. In these systems, flue gas is heated from 300°F to 800°F for catalytic conversion and absorption. In order to operate the integrated Cat-Ox process on a commercial basis, it is necessary to install the system at plant construction and this has not been done on a large scale to date. However, although the Integrated Cat-Ox process has not been operated large scale, the technical viability of the catalytic conversion and absorption steps have been tested in the Reheat process. The hot electrostatic precipitators have been tested independently. Thus, although the Integrated Cat-Ox process has not been fully tested at the 110 Mw level, its components have been so tested.

The Wood River Plant (Illinois Power) encountered several problems and operation has been discontinued at this time. These problems included poor accessability to viewports and controls, insufficient personnel training, extensive time required to isolate the Cat-Ox system, poor location of the product line, and some materials of construction problems. These problems should be solvable by design and construction changes in a newly constructed plant. Although the plant is not currently operating and is regarded by some to have been unsuccessful, engineering analysis has indicated (PA-209) that operation of the Integrated Cat-Ox process is technically feasible.

Use of Commercialized Technology - The process uses equipment that can be regarded as commercial and the process concept is not complex. It should be easily controlled when utilized in the integrated system. However, due to problems with the Wood River Plant and the fact that a large scale Integrated Cat-Ox plant has not been built to date, a demonstration plant using the process would seem to be imperative before true commercialization can be achieved.

Process Controllability - Control of the Integrated Cat-Ox process is accomplished by controlling the temperature of the acid recycle line (and thus of the absorber) and circulation rates. The process should be fairly easy to control and devices for such control are readily available in commercial markets.

ECONOMIC AND TECHNOLOGICAL CONSIDERATIONS

Economics for the Integrated Cat-Ox Process are presented in Tables 2 and 3. Capital costs for the project are estimated as \$70,875,000 or \$142 per killowatt on a mid-1979 basis. Unit revenue requirements are estimated at 3.72 mills per kwh using a utility financing method.

Since the process utilizes equipment and processing steps that are currently available, it is to be expected that the process is not very sensitive to technological factors in terms of economics. It should be kept in mind, however, that the reliability of the economic estimates must be considered as lower than those for a more developed or commercial process due to the lack of operation of a large scale Integrated Cat-Ox unit to date.

Table 2

Catalytic Oxidation Process

Total Capital Investment Analysis[a]

	Investment, $
Direct Investment	
Converter and absorber startup bypass ducts and dampers	799,000
Electrostatic precipitators and inlet ducts (4 high temperature electrostatic precipitators including common feed plenum)	13,659,000
Sulfur dioxide converters and ducts (4 converters including catalyst sifter, hopper, storage bin, conveyors, and elevators)	3,352,000
Heat recovery and ducts (4 steam/air heaters and 4 fluid/air heaters including ducts between economizers and air heaters, and combustion air ducts and damper between powerhouse and air heaters; investment credit for use of smaller air heaters included)	2,234,000
Fans (4 ID fans including exhaust gas ducts and dampers between ID fans and stack gas plenum)	2,212,000
Sulfuric acid absorbers and coolers (2 absorbers including mist eliminators, coolers, tanks, pumps, and ducts and dampers between air heaters and ID fans)	14,606,000
Sulfuric acid storage (storage and shipping facilities for 30 days production of H_2SO_4)	599,000
Subtotal	37,461,000
Services, utilities, and miscellaneous	2,248,000
Total direct investment	39,709,000
Indirect Investment	
Engineering design and supervision	1,071,000
Architect and engineering contractor	268,000
Construction expense	5,309,000
Contractor's fees	1,576,000
Total indirect investment	8,224,000
Contingency	9,587,000
Total fixed investment	57,520,000
Other Capital Charges	
Allowance for startup and modifications	5,752,000
Interest during construction	6,902,000
Total depreciable investment	70,174,000
Land	25,000
Working capital	689,000
Total capital investment	70,888,000

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a. Basis:

New 500-MW coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).
Coal properties: 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Investment requirements for disposal of fly ash excluded.
90% SO_2 removal.

Table 3
Catalytic Oxidation Process
Revenue Requirements Analysis[a]

	Annual quantity	Unit cost, $	Total annual amount, $
Direct Costs			
Raw material			
Catalyst	113,100 liters	2.50/liters	282,800
Total raw materials cost			282,800
Conversion costs			
Operating labor and supervision	7,890 man-hr	12.50/man-hr	98,600
Utilities			
Steam	189,000 M lb	2.00/M lb	378,000
Heat credit	987,000 MM Btu	-1.25/MM Btu	(1,233,800)
Process water	312,000 M gal	0.12/M gal	37,400
Electricity	91,199,000 kwh	0.029/kwh	2,644,800
Maintenance, 4% of total direct investment			1,588,400
Analyses	4,000 man-hr	17.00/man-hr	68,000
Total conversion costs			3,581,400
Total direct costs			3,864,200
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6% of total depreciable investment			4,210,400
Average cost of capital and taxes at 8.6% of total capital investment			6,096,400
Overhead			
Plant, 50% of conversion costs less utilities			877,500
Administrative, 10% of operating labor			9,900
Marketing 10% of sales revenue			242,000
Total indirect costs			11,436,200
Gross annual revenue requirements			15,300,400
Byproduct Sales Revenue			
Sulfuric acid	121,000 tons	20.00/ton	(2,420,000)
Total annual revenue requirements			12,880,400

	Dollars/ton coal burned	Mills/kwh	Cents/million Btu heat input
Equivalent unit revenue requirement	8.59	3.68	40.9

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a. Basis:
New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up).
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned: 1,500,000 tons/yr, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Total capital investment, $70,888,000; total depreciable investment, $70,174,000; total direct investment, $39,709,000.
Investment and revenue requirements for disposal of fly ash excluded.
90% SO_2 removal.

APPLICABILITY

Suitability for Utility Applications - The Integrated Cat-Ox process is suitable only for new plant construction. An adaptation of the process, the Reheat Cat-Ox process, can be retrofitted. However, the Reheat Process requires reheat of the flue gas to 800°F for catalytic conversion. This energy loss would be costly. Thus, the process does not appear favorable in retrofit situations and is evaluated here only in the integrated mode. The process cannot be decoupled. The process is relatively simple in concept and thus should be fairly acceptable to the utility industry.

A potential problem that could affect the applicability of the process is marketability of the product sulfuric acid. It appears to be suitable only for fertilizer production for two reasons; it is dilute and it contains trace elements. The acid is too dilute for most industrial applications and cannot compete with conventional sources of concentrated sulfuric acid. The trace elements in the acid may also make it unsuitable for industrial application. However, these factors should not hinder use in fertilizer manufacture. Such streams from the secondary nonferrous metals industry have proven suitable for these applications.

Suitability for Industrial Application - The above comments are relevant to industrial applicability. Modularization of the process does not appear particularly advantageous due to the process' relative simplicity. It does appear applicable to small boilers. Location in an industrial complex could assist in finding end use for the product sulfuric acid.

Flexibility to Provide Alternate Products - Flexibility is poor since sulfuric acid is the only product that can be produced.

Regional/Site Considerations - The process appears to have potential limitations in the area of site selection. It would seem imperative that an outlet for the dilute sulfuric acid product be found. This will potentially be site dependent due to the characteristics of the acid.

PROCESS ALTERNATIVES

Two Stage Absorption - Use of a two stage absorption system would increase both the sulfur trioxide removal and acid concentration. In such a system, the lower stage would operate at a higher temperature and thus produce a more concentrated acid. The upper stage would be operated at a lower temperature and produce a less concentrated acid stream and an acceptable flue gas H_2SO_4 carry-over. This system could produce an 87% sulfuric acid.

However, there is some question as to the desirability of this alternative. An 87% acid is not much more valuable than the 78% acid made under the original system and would be produced at a cost of greater operating complexity and larger capital expenditures.

Start-up Procedure - If started up with water as absorbent, the process initially produces a dilute sulfuric acid. The corrosive nature of this dilute acid requires that the system be built of more expensive materials of construction that are required for only a short time. Analysis has indicated that start-up of the system with a 98% sulfuric acid stream would allow use of less expensive materials of construction. This would seem to be a viable alternative through which capital costs could be reduced with only a slight increase in operating costs.

SUMMARY

The Integrated Cat-Ox process seems to be a viable FGD Process. Although the process appears to be fairly capital intensive, operating costs are low compared to other processes. Operation of the system is not complex and the process produces a marketable sulfuric acid product. For these reasons, the process appears fairly attractive for further development.

A major problem with the process is that although the various parts of the process have been demonstrated, the Integrated Cat-Ox process has not been operated on a large scale. This will require installation on a new, probably baseload power plant at the construction stage in contrast to most other FGD systems which can be retrofitted to older, low utilization units. Consequently, use of the integrated Cat-Ox process would involve significant economic risk to an individual utility or industrial concern. However, this step is imperative in development of the process to commercialization.

References - BE-326, OT-028, PA-029.

KURABO AMMONIUM SULFATE PROCESS

In the Kurabo process, SO_2 is absorbed in an acidic solution of ammonium sulfate. With the solution pH maintained below 4, the partial pressure of ammonia is quite low so that ammonia plume formation is not the problem with this process that it is in other ammonia scrubbing processes. A KBCA unit is used to precool the flue gas and concentrate the ammonium sulfate solution. SO_2 is then absorbed in a packed tower. The KBCA is a special multi-jet scrubber developed by Kurabo for sodium salt scrubbing. A conventional countercurrent type of scrubber could probably be used instead of a KBCA. In the KBCA, flue gas is scrubbed with ammonium sulfate solution from the main scrubber. The ammonium sulfate solution contains sulfite that was absorbed in the packed tower. The gas is cooled and the scrubbing solution concentrated by evaporation of water. Flue gas is then countercurrently contacted with recycle ammonium sulfate in the main absorber, reheated, and sent to the stack. Concentrated ammonium sulfate/sulfite solution is then oxidized with air to convert the absorbed sulfite into sulfate. Oxidized solution is recycled to the main absorber. A portion of the oxidized liquor is treated with lime to precipitate gypsum and produce ammonium hydroxide (NH_4OH). The ammonium hydroxide is recycled to the oxidizer to adjust the pH of the solution to 3 to 4. A simplified flow diagram of the Kurabo ammonium sulfate/gypsum process is given in Figure 1.

The process can be operated to produce ammonium sulfate rather than gypsum as a by-product. For this mode of operation the ammonium sulfate concentration would be kept high, probably about 3 molar, to minimize the amount of water to be evaporated.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - SO_2 removal efficiencies of 95% have been achieved with systems producing gypsum as a by-product. More than 98% SO_2 removal has been attained with a small unit that produces ammonium sulfate as a by-product.

Multipollutant Control - The process does not appear to have potential for NO_x removal. Some particulate removal has been reported in operation of units on oil-fired boilers.

Secondary Pollution Problems; Air - Formation of an ammonia plume, which causes serious secondary air pollution problems in other ammonia scrubbing processes, is avoided in the Kurabo process because of the low pH of the scrubbing liquor. Volatile ammonium hydroxide evolved in the regeneration step may present on-site problems unless adequate containment or venting is practiced.

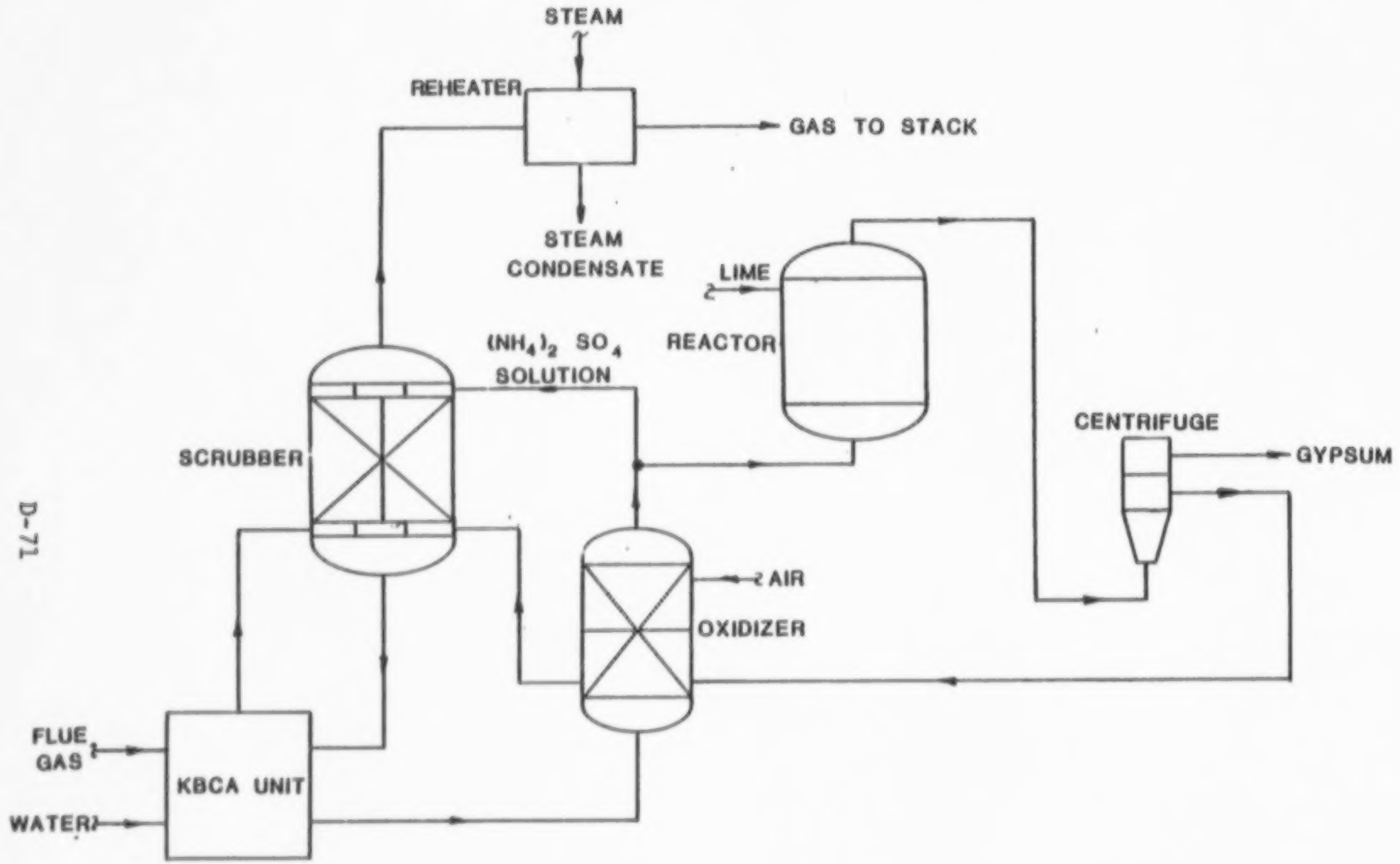
STEAM
REHEATER
GAS TO STACK
STEAM CONDENSATE
LIME
REACTOR
$(NH_4)_2SO_4$ SOLUTION
SCRUBBER
CENTRIFUGE
GYPSUM
AIR
OXIDIZER
FLUE GAS
KBCA UNIT
WATER

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR KURABO PROCESS

Secondary Pollution Problems; Water - A purge stream of $CaCl_2$ or NH_4Cl may be required to prevent chloride buildup. The stream would be treated by neutralization and filtration before disposal.

Secondary Pollution Problems; Solids - Unless the process is operated to produce ammonium sulfate, gypsum solid waste will be produced. Gypsum of marketable quality can be produced, but probably could not be sold in the U.S. The gypsum produced is a more desirable waste product than the calcium sulfite/sulfate sludge produced by lime/limestone processes. Gypsum is more easily dewatered, is less thixotropic, and has a greater bearing strength than calcium sulfite. Gypsum is suitable for landfill disposal.

Energy Intensiveness - Values of operating parameters were not available for all areas of the Kurabo process. Raw material and utility requirements were estimated based on the following assumptions:

- L/G: 60 gal/1000 scf
- Oxidation: 5 times stoichiometric amount of air at pressure of 28 psi
- Lime consumption: 1.0 mole/mole SO_2 removed; 95% CaO
- Ammonia makeup: 0.03 moles/mole SO_2 removed

The Kurabo process is similar to the Dowa process. Comparable values of L/G and pressure drop have been reported for the two processes, and energy requirements for other processing areas such as particulate removal, raw material handling, slurry processing, and solids disposal should be similar for the two processes. The Kurabo process would have lower energy requirements for feed preparation since it uses lime for regeneration rather than limestone. Energy requirements for the Kurabo process may thus be slightly lower than those for the Dowa process, but still significantly higher than for the lime/limestone or sodium double alkali processes. Results of the raw material and utility calculations are given in Table 1.

If ammonium sulfate, rather than gypsum, is produced as a byproduct, the requirement for lime will be eliminated. Ammonia consumption will be increased to about 6.1 tons/hr, and about 23.6 tons/hr of ammonium sulfate will be produced for the base case. Additional energy will be required to crystallize the ammonium sulfate.

TABLE 1. RAW MATERIAL AND UTILITY REQUIREMENTS FOR KURABO AMMONIUM SULFATE PROCESS

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (dry)

Raw Materials [1]		
Lime	tons/hr	10.4
Ammonia	lb/hr	180
Utilities		
Process Water[2]	10^3 gal/hr	30.2
Electricity	kw	
Gas Handling		6150
SO Absorption		2650
Oxidation		1450
Miscellaneous[3]		3130
Steam	10^6 Btu/hr	51.1
Solid Waste	tons/hr	31.2

[1] Not including raw materials for chloride purge.
[2] Not including purge.
[3] Includes particulate removal, raw material handling, slurry processing, solids disposal.

DEVELOPMENT STATUS

Overall Status - Five applications of the Kurabo process to oil-fired industrial boilers representing about 200 Mw equivalent generating capacity (356,000 scfm) have been put into operation in Japan since 1974. These units produce gypsum as a by-product Another small unit (5 Mw equivalent) producing ammonium sulfate was put into operation in 1976. The process has been integrated at these plants.

Use of Commercialized Technology - This process uses technology common to other FGD systems. A "KBCA" scrubber, previously developed by Kurabo, is used to precool the flue gas and concentrate the scrubber solution, but a countercurrent scrubber could be used instead. Thus, the process uses commercially available technology.

Process Controllability - Control of pH is important in this process. Scrubber pH is maintained at around 3-4. At pH less than 4, the partial pressure of ammonia is quite low so that plume formation is not a problem. At pH less than 3, serious corrosion problems may be encountered. The best conditions for oxidation also occur in a pH range of 3-4. Since the pH of the scrubbing liquor exiting the absorber is decreased by the absorption of SO_2, the pH is adjusted up to the 3 to 4 range by the addition of ammonium hydroxide from the regeneration reaction. Oxidation occurs fairly rapidly, with about five times the stoichiometric amount of air used. Small amounts of vanadium and iron derived from the combustion are presumed to catalyze the oxidation reaction.

The amount of water that must be added to the system to wash gypsum and dissolve calcium hydroxide is less than that evaporated by the hot flue gas and exiting with the gypsum product. Thus, the process could be operated "closed loop", with additional makeup water added to the precooling-concentration tower. In this mode of operation, however, chlorides may build up in the system. A purge stream of $CaCl_2$ or NH_4Cl solution may be necessary.

Volatile ammonium hydroxide is evolved during the regeneration reaction. Adequate containment or venting is necessary to prevent ammonia fumes from escaping in the vicinity of the regeneration reactors.

In summary, although the process must operate in a fairly narrow pH range, control problems are not expected to be serious.

ECONOMIC AND TECHNOLOGICAL FACTORS

A detailed capital cost estimate for the Kurabo process was not performed due to unavailability of data. Since the equipment required is similar to that required for the Dowa process, capital costs for the two processes should be similar. The use of the KBCA may add to the capital cost, especially if it is required along with additional units for particulate removal. Costs for reactors may be somewhat less, however, since lime (which is generally more reactive than limestone) is used for regeneration. Operating costs for Kurabo would probably be higher than those for Dowa because of the higher cost for lime. Electricity cost (which is the major contributor to direct operating cost for Dowa) may be slightly lower for Kurabo, but the cost for lime for the Kurabo process would tend to offset this saving.

Capital costs for a Kurabo process designed to produce ammonium sulfate would probably be somewhat lower than those for a process designed to produce gypsum since equipment such as the lime reactors and solids handling and disposal equipment would not be required. Equipment to dewater and crystallize the ammonium sulfate would be required, however. Raw material costs would be higher for the ammonium sulfate-producing process because of the increased ammonia requirements. Energy costs may also increase due to the crystalization requirement. However, overall operating costs could be lower since the ammonium sulfate could be sold and the need for gypsum disposal would be eliminated.

APPLICABILITY

Suitability for Utility Application - The process should be suitable for utility application. Retrofits should be relatively easy, but perhaps slightly more difficult than for sodium double alkali because of the higher L/G and the requirement for an oxidizer in the scrubber loop. The load following capability of the scrubber should be adequate. The regeneration system could be decoupled from the absorption section through use of intermediate storage, but the oxidizer and scrubber would be difficult to separate. The gypsum by-product could probably not be marketed in the U.S.; land would be needed for disposal. Ammonium sulfate might be marketable as fertilizer in certain areas.

Suitability for Industrial Application - Considerations for retrofitability, by-product utilization, and separability of process steps are similar to those for utility application. The process should be adaptable for modularization in all areas of the process. It has been applied to relatively small boilers.

Flexibility to Provide Alternate Products - Either gypsum or ammonium sulfate can be produced.

Regional/Site Considerations - This process should be suitable over a broad range of applications. It may be favored in certain areas where a market for ammonium sulfate exists. Applicability may be somewhat limited in certain locations by the need for gypsum disposal.

PROCESS ALTERNATIVES

Free Sulfite - Because ammonium sulfate solution does not have a high capacity for SO_2, a relatively high L/G is required to achieve good SO_2 removal. The SO_2 absorption capacity of the scrubbing liquor could be improved by recycling part of the scrubbing liquor back to the absorber without oxidizing it so that some free sulfite is present in the liquor. The absorption capacity of the liquor could also be improved by adding an organic buffer such as adipic acid. However, these measures would increase the pH of the scrubbing liquor (to about 5), and thus increase the possibility of plume formation.

Concentrated Ammonia Solution - In other ammonia scrubbing processes, such as the NKK process developed by Nippon Kokan Kabushiki Kaisha, SO_2 is scrubbed with a more concentrated, higher pH ammonia solution. Forced oxidation takes place outside the scrubber loop so that the scrubbing solution contains sulfite/bisulfite rather than sulfate. The scrubbing solution thus has a greater capacity for SO_2 than the more dilute, acidic ammonium sulfate solution used in the Kurabo process, and a lower L/G is required to achieve good SO_2 removal. Like the Kurabo process, the NKK process can produce either ammonium sulfate or gypsum as a by-product. Because of the higher concentration in the scrubber solution, a more concentrated ammonium sulfate product is produced. Ammonia plume formation can be a serious problem with this process, but may be controlled by a wet electrostatic precipitator after the scrubber. This precipitator would increase capital costs of the system.

SUMMARY

The Kurabo process can tolerate any level of scrubber oxidation without requiring a sulfate purge or a complex operation for sulfate removal. High quality gypsum is produced as a by-product rather than calcium sulfite sludge. In areas where ammonium sulfate can be marketed, the lime neutralization step can be eliminated and ammonium sulfate, rather than gypsum, produced as a by-product. The Kurabo process may be superior to other ammonia scrubbing processes since the low pH scrubbing liquor suppresses plume formation. It does, however, require a higher L/G than the sodium double alkali process. Possible areas for further research include investigation of operation in the free sulfite mode or addition of an organic acid buffer to improve SO_2 absorption capacity.

References - AN-056, AN-147, AN-187, PE-182, RO-190, YO-058.

LIME/LIMESTONE WET SCRUBBING PROCESS

The lime and limestone FGD systems have been considered together as they are similar in design, process chemistry, and operating problems. Major differences between these two process types will be noted where appropriate.

The absorption of SO_2 from flue gases by a lime or limestone slurry constitutes a multiphase system involving gas, liquid, and solids. The chemistry is quite complex, involving many side reactions. The overall reactions are those of SO_2 with lime (CaO) or limestone ($CaCO_3$) to form calcium sulfite ($CaSO_3$) with some oxidation of the sulfite to form calcium sulfate ($CaSO_4$). These reactions can be represented as follows:

Lime

$$SO_{2\,(g)} + CaO_{(s)} + \tfrac{1}{2}H_2O \rightarrow CaSO_3\cdot\tfrac{1}{2}H_2O_{(s)}$$

$$SO_{2\,(g)} + \tfrac{1}{2}O_2(g) + CaO_{(s)} + 2H_2O \rightarrow CaSO_4\cdot 2H_2O_{(s)}$$

Limestone

$$SO_{2\,(g)} + CaCO_{3\,(s)} + \tfrac{1}{2}H_2O \rightarrow CaSO_3\cdot\tfrac{1}{2}H_2O_{(s)} + CO_{2\,(g)}$$

$$SO_{2\,(g)} + \tfrac{1}{2}O_{2\,(g)} + CaCO_{3\,(s)} + 2H_2O \rightarrow CaSO_4\cdot 2H_2O_{(s)} + CO_{2\,(g)}$$

The calcium sulfite and sulfate crystals precipitate in a reaction vessel or hold tank which is designed to provide adequate residence time for solids precipitation as well as for dissolution of the alkaline additive. The hold tank effluent is recycled to the scrubber to absorb additional SO_2. A slip stream from the hold tank is sent to a solid-liquid separator to remove the precipitated solids from the system. The waste solids, which may vary from 35-70 weight percent solids, are generally disposed of by ponding or landfill. A simplified flow diagram is presented in Figure 1.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - The SO_2 removal efficiency of lime/limestone systems will depend on a number of important factors including contactor design, L/G, and inlet SO_2 concentration. Removal efficiencies of greater than 90% have been demonstrated on commercial units. This removal level can be attained with a system properly designed for site specific requirements. Better

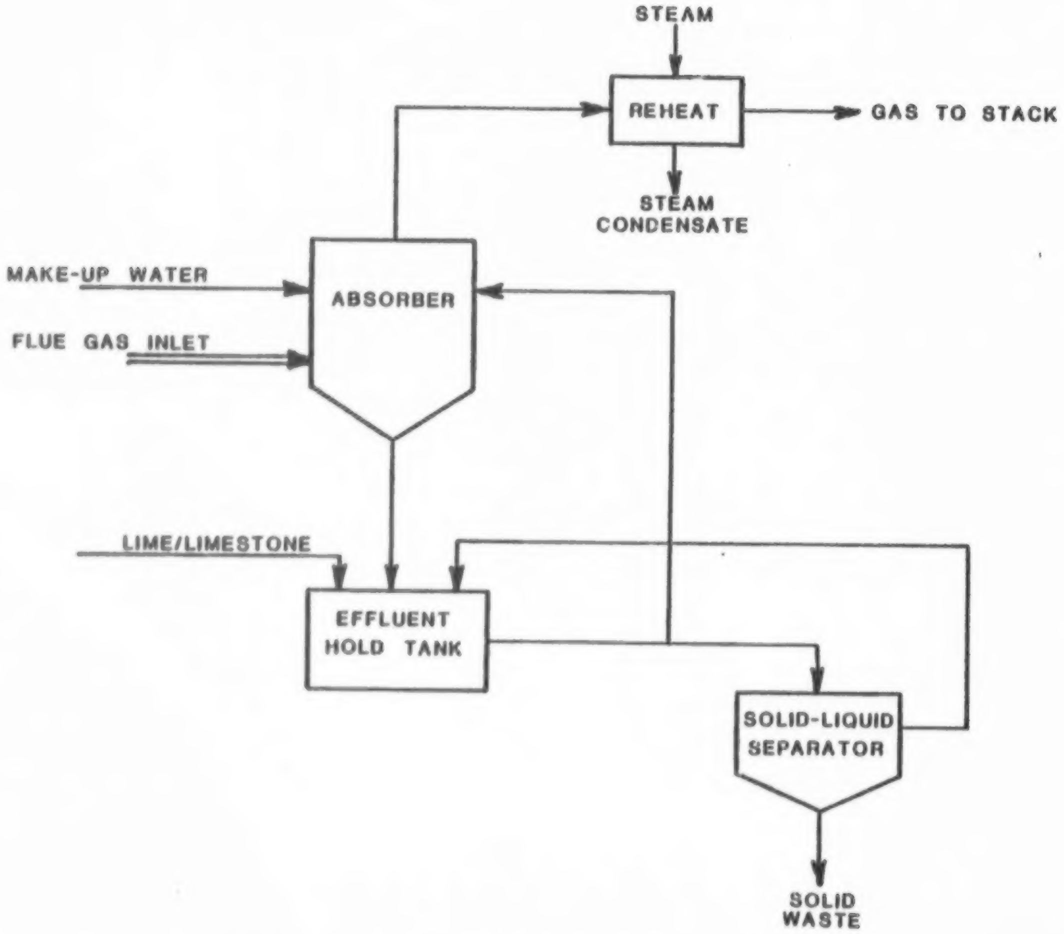
STEAM
REHEAT
GAS TO STACK
STEAM CONDENSATE
MAKE-UP WATER
ABSORBER
FLUE GAS INLET
LIME/LIMESTONE
EFFLUENT HOLD TANK
SOLID-LIQUID SEPARATOR
SOLID WASTE

FIGURE 1. SIMPLIFIED LIME/LIMESTONE WET SCRUBBING PROCESS FLOW DIAGRAM.

02-2176-1

removal may be achieved by the use of additives such as MgO and organic acids.

Multipollutant Control - Particulates can be removed concurrently with SO_2 in lime/limestone systems. Depending on scrubber design, particulate removal efficiencies greater than 99 percent can be achieved. Venturi contactors have been successfully operated as particulate/SO_2 scrubbers at several installations. However, more efficient SO_2 contactors are available which operate at lower gas phase pressure drops. Nitrogen oxides are not removed.

Secondary Pollution Problems; Air - No secondary air pollution problems are associated with lime/limestone scrubbing.

Secondary Pollution Problems; Water - Soluble species and trace elements can be leached from the waste solids, causing water pollution problems. Alternatives for prevention of leaching include disposal of the solids in a lined pond and stabilization of the sludge. Lining the disposal pond with a material impervious to water will prevent leachable materials from leaving the pond by seepage, but rain and subsequent runoff must be considered in locating the pond. Ideally, stabilized sludge should be resistant to leaching.

Secondary Pollution Problems; Solids - One of the main disadvantages of lime/limestone systems is the requirement for disposal of the waste product. The quantity of sludge produced is large in weight and volume, and requires a large waste pond or landfill area for disposal. As noted earlier, leaching of soluble species and trace elements from the sludge can be a problem. To improve the quality of the waste product, work is continuing in the area of sludge stabilization. Ideally, stabilized sludge should be structurally stable as well as resistant to leaching. Sludge stabilization requires additional processing and materials such as lime or dry fly ash.

Energy Intensiveness - Material and energy balance calculations were based on use of a Turbulent Contact Absorber (TCA). In addition, the following values for operating variables were assumed:

- Stoichiometry - 1.1 moles CaO/mole SO_2 sorbed for a lime system and 1.3 moles $CaCO_3$/mole SO_2 inlet for a limestone system
- L/G - 60 gal/1000 scf for lime and 70 gal/1000 scf for limestone
- Oxidation fraction - 0.15 moles sulfate formed/mole SO_2 sorbed for lime versus o.25 moles sulfate/mole SO_2 sorbed for limestone

- No heat loss in stack after reheat
- Lime composition - 95% CaO, 5% inerts:
  Limestone composition - 90% $CaCO_3$, 5% inerts, 5% H_2O.

Raw material and utility requirements for the lime and limestone systems are presented in Table 1.

TABLE 1. RAW MATERIAL AND UTILITY REQUIREMENTS FOR LIME/LIMESTONE SCRUBBING SYSTEMS

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (Dry)

		Limestone Systems	Lime Systems
Raw Materials			
Limestone	(tons/hr)	29.3	-
Lime	(tons/hr)	-	12.0
Utilities			
Process Water	(10^3 gal/hr)	43.6	40.7
Electricity			
Pumps	(kw)	3260	2790
Fan	(kw)	6210	6210
Particulate Removal	(kw)	1100	1100
Limestone Preparation	(kw)	750	(1)
Steam	(MM Btu/hr)	48.4	48.4
Solid Waste	(tons/hr)	85.1	65.7

(1) Lime assumed to be purchased in form suitable for SO_2 absorption.

The major difference between the systems is in the amount of lime and limestone used to remove SO_2. The higher cost for lime, however, will tend to offset its lower consumption rates.

There is little difference between the two systems in the remaining raw material and utility requirements. The differences in electricity consumption are due to limestone preparation and lower L/G for the lime system. L/G for lime scrubbing could be lower than presented and this would further reduce electricity requirements. An L/G of 40, for example, would result in pumping requirements of 1860 kw rather than 2790 kw. Steam requirements for reheat are identical in both cases. The slight variance in process water requirements is due to the different amounts of water disposed of with the waste sludge. Because of the lower utilization of limestone, more waste is produced from a limestone system than from a lime system, and more water is thus lost in the waste sludge of limestone systems. These calculations assume the use of a pond for thickening and disposal with a final solids concentration of 40 percent. A higher solids content (approximately 50% for limestone systems and 45% for lime) can be achieved by using a thickener, as shown in the flow diagram in Figure 1. Water consumption can thus be decreased.

The lime and limestone scrubbing processes have relatively low energy requirements. As with other wet scrubbing processes, a significant amount of energy is required for gas reheat, but, like other throwaway processes, no energy is required for regeneration. Energy requirements are higher than those for the sodium double alkali process because of the higher L/G required.

DEVELOPMENT STATUS

Overall Status - Lime/limestone systems have been commercially demonstrated with varying degrees of success at several utility power stations. As of April 1977 there were 24 operational lime/limestone FGD systems in the U.S. treating flue gas from 5997 Mw of electrical generating capacity. In addition, the majority of FGD systems in planning and construction stages are lime/limestone. This is because lime/limestone systems are the most technically advanced and usually the most economically attractive. However, this does not imply that all operating problems have been eliminated.

Use of Commercialized Technology - Generally speaking, no special or unique process equipment is required for lime/limestone scrubbing. All of the equipment has been operated and the systems have been fully integrated in the early demonstration units.

Process Controllability - Several problems have become evident with operation of full-scale systems. Problem areas such as chemical scaling, plugging, sludge quality, and variable SO_2 removal efficiency emphasize the need for good process control.

Chemical scaling in the absorber was one of the first problems encountered. In general, scrubber design has moved toward elimination of internals to alleviate the scaling and plugging problems. A relatively good understanding of the causes of chemical scaling has been developed and current process designs should reduce this problem. Calcium sulfate scaling has presented the most severe problems. In general, calcium sulfite scaling has been reduced by controlling the pH of the liquor in the scrubber. By maintaining sufficient hold tank residence time and L/G's, the scrubbing liquor can be desupersaturated enough such that the sulfite and sulfate pick-up in the scrubber do not result in scaling. Addition of magnesium to lime/limestone systems has been shown to have a positive effect on scale control as well as SO_2 removal. It has been verified that sulfate is coprecipitated with calcium sulfite to form a solid solution. Approximately 0.15 moles of sulfate per mole of sulfur can exist in the solid solution. If the oxidation fraction is maintained below 0.15 moles sulfate/mole SO_2 sorbed, the system can be designed to operate in a subsaturated calcium sulfate mode and calcium sulfate scaling should not be a problem. This mode of operation is generally not feasible with systems where greater than 15 percent oxidation is expected. Generally, higher oxidation will prevail with flue gas containing less than 1000-2000 ppm SO_2.

Mist eliminator plugging and scaling have also presented problems. Potential solutions include frequent washing with the maximum amount of makeup water being employed in demister washing. High pressure washing has also been employed. Proper control of pH to minimize excess limestone has also been successful. However, demister plugging is a continuing problem. Reentrainment of droplets is also of concern.

The disposal of large quantities of sludge presents a severe problem for lime/limestone FGD systems. High calcium sulfite concentration sludges tend to be thixotropic and are not easily dewatered. Advancements in sludge stabilization and identification of disposal options are receiving maximum effort now in continuing lime/limestone process development.

ECONOMIC AND TECHNOLOGICAL FACTORS

Estimates of capital and operating costs for the limestone wet scrubbing process are given in Tables 2 and 3, respectively. Capital costs for the limestone process have been established at $47,949,000 with annual revenue requirements of $14,945,000 or 4.27 mills/kwh based upon utility financing. Lime systems may have somewhat lower capital costs, but higher operating costs than limestone systems. The higher cost for lime may more than offset its lower consumption rate.

APPLICABILITY

Suitability for Utility Application - The principal factor to be considered when assessing a lime/limestone system's applicability in a retrofit situation is available land. The area required for sludge disposal is quite large and in some cases is equal to

Table 2

Limestone Slurry Process

Total Capital Investment Analysis[a]

	Investment, $
Direct Investment	
Limestone receiving and storage (hoppers, feeders, conveyors, elevators, and bins)	626,000
Feed preparation (feeders, crushers, elevators, ball mills, tanks, agitators, and pumps)	1,424,000
Particulate removal (4 venturi scrubbers, tanks, agitators, pumps, and common feed plenum)	5,126,000
Sulfur dioxide scrubbers (4 TCA scrubbers including a saturator, mist eliminator, effluent hold tanks, agitators, and pumps)	7,629,000
Stack gas reheat (4 indirect steam reheaters)	1,014,000
Gas handling (4 fans including exhaust gas ducts and dampers between fan and plenum)	1,366,000
Solids disposal (feed tank, pumps)	751,000
Subtotal	17,936,000
Services, utilities, and miscellaneous	1,076,000
Total process areas excluding pond construction	19,012,000
Pond construction	6,524,000
Total direct investment	25,536,000
Indirect Investment	
Engineering design and supervision	1,557,000
Architect and engineering contractor	349,000
Construction expense	3,498,000
Contractor's fees	1,126,000
Total indirect investment	6,530,000
Contingency	6,413,000
Total fixed investment	38,479,000
Other Capital Charges	
Allowance for startup and modifications	3,196,000
Interest during construction	4,617,000
Total depreciable investment	46,292,000
Land	490,000
Working capital	1,167,000
Total capital investment	47,949,000

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[a] **Basis:**

New 500-Mw coal-fired power unit (30-yr life).

Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).

Coal properties: 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu/lb.

Stack gas reheat to 175°F by indirect steam reheat.

Investment requirements for disposal of fly ash excluded.

90% SO_2 removal; wet venturi particulate removal.

Table 3
Limestone Slurry Process

Total Annual Revenue Requirements Analysis[a]

	Annual quantity	Unit cost, $	Total annual amount, $
Direct Cost			
Raw materials			
Limestone	207,295 tons	7.00/ton	1,451,100
Total raw materials cost			1,451,100
Conversion			
Operating labor and supervision	21,920 man-hr	12.50/man-hr	274,000
Utilities			
Steam	339,000 MM Btu	2.00/MM Btu	678,000
Process water	305,400 M gal	.12/M gal	36,600
Electricity	79,238,000 kwh	0.029/kwh	2,297,900
Maintenance, 8% of direct investment			2,042,900
Analyses	3,040 man-hr	17.00/man-hr	51,700
Total conversion costs			5,381,100
Total direct costs			6,832,200
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6% of total depreciable investment			2,777,500
Average cost of capital and taxes at 8.6% of total capital investment			4,123,600
Overhead			
Plant, 50% of conversion costs less utilities			1,184,300
Administrative, 10% of operating labor			27,400
Total indirect costs			8,112,800
Total annual revenue requirements			14,945,000

	Dollars/ton coal burned	Mills/kwh	Cents/million Btu heat input
Equivalent unit revenue requirement	9.96	4.27	47.4

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a. Basis:
New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up).
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned: 1,500,100 tons/yr, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Total capital investment, $47,949,000; total depreciable investment, $46,292,000; total direct investment, $25,536,000.
Investment and revenue requirements for disposal of fly ash excluded.
90% SO_2 removal; wet venturi particulate removal.

the area required for the power plant. This is a key consideration particularly when the utility is located in a densely populated area. The load-following capability of a lime/limestone process should be adequate.

In choosing materials of construction for a lime/limestone system, erosion and corrosion must be considered. Since a 10-15 percent slurry is recirculated, pumps should be erosion resistant. The scrubber material should be resistant to acid attack since it is exposed to an acid environment. Particular attention should be paid to the predicted chloride concentrations in the slurry and materials chosen accordingly. The process steps can be separated by having adequate storage between process units.

Suitability for Industrial Application - Considerations affecting retrofittability and by-product utilization for industrial applications are similar to those for utility application. The process should be applicable to small boiler operations. The process steps could be modularized but only the absorber would seem to present sufficient reliability problems to justify extensive modularization.

Flexibility to Provide Alternate Products - The process produces calcium sulfite sludge, but can be modified to produce gypsum.

Regional/Site Considerations - The raw materials are readily available in most areas, but the availability of land for sludge disposal could limit applicability.

PROCESS ALTERNATIVES

The technology, as summarized in this report, can be regarded as established and commercially available. However, as with all new technologies, attempts are constantly being made to improve the overall performance of the process or to reduce its costs. The use of mass transfer additives plus two additional process alternatives that may offer improvements are briefly described in this section.

Mass Transfer Additives - Additives such as MgO, Na_2CO_3, and organic acids can be used to improve mass transfer in lime/limestone systems, thus improving SO_2 removal, increasing limestone utilization, and permitting the use of very simple scrubber types (such as cocurrent scrubbers). SO_2 removal can be increased from 90 to 99% or limestone utilization can be improved from 1.3 moles/mole SO_2 to 1.1 moles/mole SO_2 through use of these additives. The improvement in limestone utilization also improves operability, since excess limestone (which can cause plugging of the mist eliminator) is minimized. The same degree of SO_2 removal can be achieved in a venturi scrubber with additives as in a three stage TCA without additives.

Selection of the proper additive is very important. MgO has been tested extensively with lime and limestone scrubbing. The most attractive organic acids are probably adipic, acrylic, or glyoxylic, but only benzoic acid has been tested. The alkali additives - MgO, Na_2CO_3, or NH_3 - are most effective in systems that are unsaturated with respect to gypsum because of low oxidation; they may contribute to scaling in supersaturated systems. Na_2CO_3 is more expensive than MgO, but magnesium affects gypsum crystallization while sodium does not. Organic additives would be cheaper than alkali additives under conditions of calcium sulfate saturation and possibly in subsaturated conditions when a high chloride coal is used. With alkali additives, a sufficient quantity must be added to balance the chlorides and provide excess to enhance mass transfer. Extra additive to balance chlorides is not required with the organic additives.

A disadvantage in the use of additives is the loss of additive in the waste solids. This can add to the operating cost of the system and contribute to waste disposal problems. Additive losses depend on solids handling procedures, and can be minimized in systems using forced oxidation. Thus, additives are particularly attractive in combination with forced oxidation. The Kawasaki MgO/lime process is an example of a process that uses both an additive and forced oxidation. Alkali additives contribute to waste disposal problems because they add to total dissolved solids (TDS) in the scrubbing liquor. Organic additives do not contribute quantitatively to TDS, but do have a biochemical or chemical oxygen demand. Volatility and toxicity are other possible problems that can arise from additives addition, but can be avoided by selection of the proper additive. Additives are most effective in applications with high sulfur coal. They are not effective with low sulfur coals because of the low concentration of SO_2 in gas from such coals. Gas phase resistance controls mass transfer in such applications, and additives affect only liquid phase resistance. Further work needs to be done to investigate the most promising additives and quantify the optimum addition rates of these additives. Unlike other potential process alternatives, additives can be tested, developed, and demonstrated in existing equipment.

Cocurrent Scrubbing - The basic concept of cocurrent scrubbing is a high-velocity scrubber resulting in massive entrainment followed by a change-of-gas-direction and a properly designed mist eliminator. The actual scrubber may use sprays, packing, or venturi principles for gas/liquid contact.

Higher gas velocities through the scrubber are possible; therefore, smaller diameter absorbers may be used. Since spray towers are generally designed for length to diameter (L/D) ratios of about 2 for good gas distribution, cocurrent operations are attractive from a liquid pumping height standpoint. In addition, the cocurrent scrubber concept may reduce the effect of plugged nozzles on gas distribution. In countercurrent designs the gas will tend to flow where the pressure drop is lowest (i.e., in the area of a plugged nozzle) which results in reduced mass transfer. However, in the cocurrent scrubber, the liquid flow imparts additional energy to the gas so gas will not tend to flow toward plugged nozzles. Instead, the gas flow should be higher in regions where the liquid flow is higher. Since poor gas distribution is a major concern, advantages in the cocurrent spray tower design, which include better gas distribution and reduced capital and operating costs, could more than offset any disadvantage of reduced mass transfer driving forces due to cocurrent gas and liquor flow.

Forced Oxidation - Forced oxidation systems are presently being marketed although further development work is being performed by EPA and others. As the name implies, forced oxidation systems increase the amount of sulfite which is oxidized to sulfate. This is generally done by sparging air into the hold tank. Potential advantages include improved waste solid characteristics and better limestone utilizations. If oxidations approaching 100 percent are achieved, the gypsum waste solid is suitable for wallboard production. The gypsum so produced from FGD systems in Japan is marketed, but potential for U.S. sales is not promising. Gypsum solids are more easily dewatered than sludges with a high concentration of calcium sulfite (the Japanese report sludges of over 90 weight percent solids in their forced oxidation systems), and are suitable for landfill disposal. A liquor purge may be necessary to control soluble species in systems that have waste products with a high solids content, but the purge would be no larger than the amount of liquor discharged with the waste solids from a system that does not use forced oxidation. From a utilization standpoint, the air sparge will tend to sweep CO_2 from the liquor allowing more limestone dissolution in the hold tank and higher utilizations. Double loop systems (a low pH loop for oxidation and a higher pH loop for better SO_2 removal) were first proposed. However, experimentation with single loop systems has been somewhat successful. A single loop is beneficial from a cost standpoint.

Forced oxidation does require energy to run the air compressors, but the cost for the increased power consumption is not excessive. Capital cost for the compressors is not high. In some processes using forced oxidation, sulfuric acid is added to the calcium sulfate to decrease pH. Low pH is not necessary, but probably desirable. The oxidation rate can be mass transfer or reaction rate controlled. Savings in capital and operating cost made possible by the easier solids disposal may offset the costs for oxidation.

One disadvantage of forced oxidation is the elimination of $CaSO_3$ solids so that they are not available for mass transfer. The use of additives to enhance mass transfer is thus attractive when used in conjunction with forced oxidation. Since forced oxidation also minimizes additive losses in the waste solids, forced oxidation and mass transfer additives are particularly attractive when used together.

Sludge Fixation - The properties of untreated sludges make them difficult to handle and transport and have caused concern about the effects of leachate on groundwater and the removal of large areas of land from productive use. FGD sludges usually contain some amount of fly ash which is the major source of trace elements in the leachate from the sludge. The nature of calcium sulfite causes the sludge to be difficult to dewater and also causes the sludge to repulp upon contact with water even after it is dried. The poor strength of the unstabilized sludge prevents it from being used as a load bearing material.

There are currently at least 16 vendor companies which offer sludge fixation processes or services. But, only two of these processes, the Dravo Calcilox Process and the IU Conversion System POZ-O-TEC Process, are sufficiently developed and tested to be commercially viable for FGD sludge fixation. The Chemfix Process will also be considered since it has been tested at the pilot plant level, but it presently suffers from a lack of experience and a higher cost than the other two more advanced fixation processes.

The Dravo process involves the addition of Calcilox, a product derived from basic, glassy blast furnace slag, to FGD sludges. The only full scale Dravo fixation operation is located at Pennsylvania Power Co.'s Bruce Mansfield plant (1828 Mw).

The IUCS system involves vacuum filter dewatering of FGD sludge followed by addition of lime, dry fly ash and other additives to produce a dry product called POZ-O-TEC which can be landfilled. One full scale (403 Mw) system is currently operating at Columbus and Southern Ohio Electric Co.'s Conesville Plant. Three additional plants totaling 1415 Mw are expected to be fully operational by November 1977.

The Chemfix process mixes a soluble silicate gel and Portland cement as a setting agent with the FGD sludge. Lime is also added if necessary for pH control. Chemfix experience with FGD scrubber sludges is limited to EPA tests conducted at Shawnee and other tests at Will County. Chemfix does have demonstrated experience with hazardous industrial and municipal wastes.

Fixation processes have demonstrated a definite increase in sludge stability which allows the landfilled area to be used productively. The leaching of contaminants from the stabilized material is reduced but could still be an environmental problem.

SUMMARY

Lime/limestone systems are the best developed and most technically advanced FGD systems for utility and industrial application. The sorbents, particularly limestone, are inexpensive and allow operation without regeneration. Early problems such as chemical scaling and plugging have been investigated and workable solutions have been found in most applications. However, the disposal of the solid waste product presents a significant problem from environmental and land requirement standpoints. Over 5 pounds of sludge are produced per pound of SO_2 absorbed

Three process alternatives, mass transfer additives, cocurrent scrubbing, and forced oxidation systems, may make lime/limestone more attractive by reducing costs and the amount of waste byproducts. These alternatives are still in the development stage and further research is needed to prove their value.

References - AE-016, MC-147, PE-259, RO-313, RO-333

MAGNESIA SLURRY ABSORPTION PROCESS

The magnesia slurry process uses a solution of magnesium hydroxide $Mg(OH)_2$ to absorb SO_2 and produce sulfuric acid as an end product. Because it is regenerative, the process requires that particulates and chlorides be removed upstream of the SO_2 absorber.

In the absorber, an aqueous slurry of magnesium hydroxide and magnesium sulfite (pH range 6.5 to 8.5) is used to absorb the SO_2 according to the following equations:

$$Mg(OH)_2 + SO_2 \rightarrow MgSO_3 + H_2O \tag{1}$$

$$MgSO_3 + H_2O + SO_2 \rightarrow Mg(HSO_3)_2 \tag{2}$$

Some of the sulfite in the system is oxidized to sulfate. The magnesium sulfite and sulfate, which are formed as hydrate crystals, are centrifuged and dried. The dried crystals are calcined to produce solid MgO and an off gas of 7-9 percent SO_2. The MgO is recycled to the process and the SO_2 is sent to a sulfuric acid plant. A flow diagram of the process is presented in Figure 1.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - The process has demonstrated the ability to remove greater than 90 percent of the SO_2 from flue gas. Tests at Boston Edison Company's Mystic Station and at PEPCO's Dickerson Station have consistently resulted in 90 percent or greater SO_2 removal using both fresh and regenerated MgO. Removal efficiencies of over 97 percent are possible.

Multipollutant Control - SO_3 removal has not been quantified although it is believed that some SO_3 is removed by the absorber. NO_x removal was not reported by the Boston Edison or Potomac Electric demonstration units. The results of a pilot plant study by Babcock and Wilcox completed in 1970 reported that the absorption of NO_x was negligible under all conditions tested using either a venturi or packed column absorber. Applications on coal-fired boilers require particulate removal upstream of the absorber. The Boston Edison oil-fired Mystic Station did not employ flue gas pretreatment and removed from 50 to 70 percent of the particulates in the venturi absorber.

Secondary Pollution Problems; Air - Some magnesium compounds may be lost out the stack with the flue gas. Particulates will also be present from the dryer and calciner operations but should be controllable with standard equipment. Fugitive dust from the handling and transfer of dry magnesium compounds may contribute to secondary air pollution.

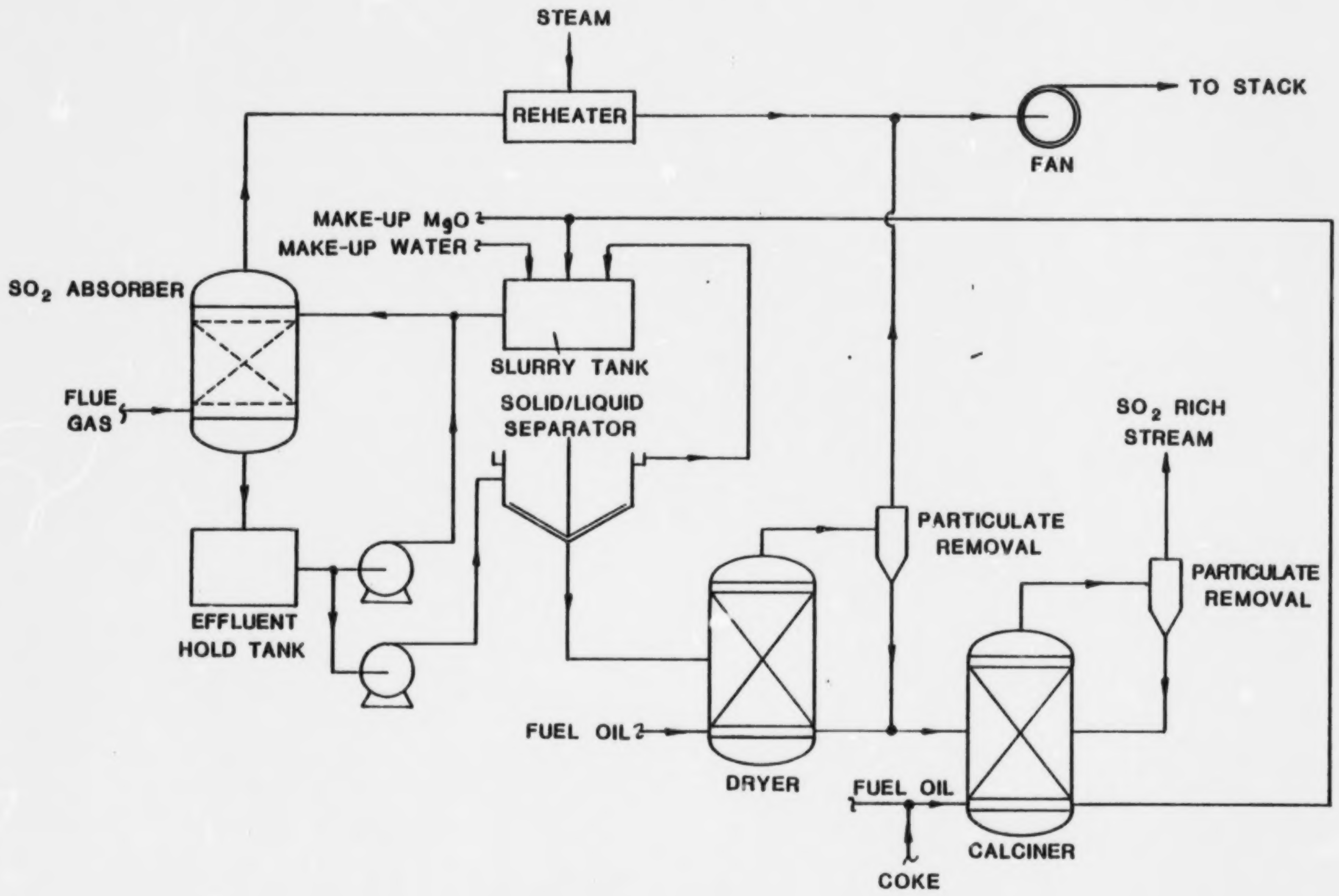
STEAM
REHEATER
TO STACK
FAN
MAKE-UP MgO
MAKE-UP WATER
SO2 ABSORBER
SLURRY TANK
FLUE GAS
SOLID/LIQUID SEPARATOR
SO2 RICH STREAM
PARTICULATE REMOVAL
EFFLUENT HOLD TANK
PARTICULATE REMOVAL
FUEL OIL
DRYER
FUEL OIL
COKE
CALCINER

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR MAGNESIA SLURRY ABSORPTION PROCESS

Secondary Pollution Problems; Water - A purge stream from the magnesia slurry process is treated for removal of impurities introduced with makeup water, fly ash in the calciner, coke and other sources as needed. Purge requirements are site specific and depend on factors such as magnesia quality, makeup water quality, and the quantity and quality of ash which enters the system.

Secondary Pollution Problems; Solid - No secondary solid pollution problems are anticipated with the magnesia slurry scrubbing process.

Energy Intensiveness - This process is relatively energy intensive in that it has a thermal regeneration step requiring about 120 x 10^6 Btu/hr of heat for drying and calcining the magnesium slurry. This heat is currently provided by No. 6 fuel oil. The potential exists for using coal as a calciner fuel if the coal ash could be readily separated from the recycle MgO product. The process also requires stack gas reheat. In addition, a small amount of coke is consumed in the calcination reaction to reduce $MgSO_4$. Low ash (less than 10 percent) coke is required to prevent excessive contamination of the recycle MgO. Raw material and energy requirements for this process are presented in Table 1.

TABLE 1. RAW MATERIAL AND ENERGY REQUIREMENTS
FOR A MAGNESIA SLURRY SCRUBBING SYSTEM

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (Dry).

		Quantity
Raw Materials		
Lime	(lb/hr)	1800
Magnesium Oxide (98%)	(lb/hr)	320
Coke	(lb/hr)	220
Utilities		
Process water	(10^3 gal/hr)	315
No. 6 Fuel Oil		
Dryer	(10^6 Btu/hr)	64
Calciner	(10^6 Btu/hr)	55
Electricity		
Scrubbing	(kw)	7750
Slurry Processing & Drying	(kw)	800
Calcination	(kw)	380
Acid Plant	(kw)	1300
Other	(kw)	140
Steam (500 psig)	(10^6 Btu/hr)	44.5
Heat Credit	(10^6 Btu/hr)	2.9

DEVELOPMENT STATUS

Overall Status -Work directed toward applying the technology of the magnesium pulping process to SO_2 scrubbing began as early as the 1930's. Researchers in different countries worked independently to develop the following three major variations of the process:

- Wet scrubbing of flue gas with a basic slurry of magnesium oxide and magnesium sulfite (Basic Slurry Process - USA and Japan, NIIOGAZ Process - USSR)
- Wet scrubbing of flue gas with a slurry of magnesium oxide, magnesium sulfite, and manganese dioxide (Grillo Process - West Germany)
- Wet scrubbing of flue gas with an acidic solution of magnesium bisulfite, magnesium sulfite, and magnesium sulfate (Clear Liquor Process - USA).

All of the unit operations used in the process are well developed. The process has been demonstrated in a completely integrated system on three commercial size (95-150Mw) retrofit units in the U.S. The Boston Edison unit was oil-fired while the Potomac Electric and Philadelphia units were coal-fired.

Use of Commercialized Technology - The processes all use operations that are commercial in the chemical processing industry.

Process Controllability - In general, control requirements for this process are not considered sensitive although the process is relatively complex mechanically. Operating problems experienced to date have been largely related to the solids handling system in that both magnesium sulfite-hexahydrate and magnesium sulfite-trihydrate may be formed in the scrubber operation. The trihydrate crystals are difficult to dewater and have resulted in operating problems when formed in systems designed to handle the larger, more easily dewatered hexahydrate crystals. Experience to date has shown that trihydrate crystals are produced from oil-fired furnaces and the hexahydrate from coal-fired applications. Work is currently underway to determine the process variables affecting the formation of the sulfite crystal types which may eventually lead to development of a method for controlling crystal formation in the system.

It is necessary to control calciner temperature so that magnesium oxide is not dead burned. Dead burning results when temperatures are too high in the calciner and magnesium oxide is melted into a refractory like material that is inactive.

ECONOMIC AND TECHNOLOGICAL FACTORS

Analysis of the magnesium oxide process indicated total capital costs of \$51,924,000. Operating costs were estimated as \$8,185,200 less \$2,300,000 for sulfuric acid sales. Unit revenue requirements were estimated at 4.26 mills/kwh using a utility financing method. The processing technology is well developed and process costs seem relatively insensitive to technological factors. The calcination step has been costed as fuel oil-fired. Coal firing could reduce these operating costs, but the additional capital costs would at least partially offset this advantage. A summary of capital and operating costs for the Magnesia Slurry process is presented in Tables 2 and 3.

APPLICABILITY

Suitability for Utility Application - Retrofit could be limited by land availability although this consideration is reduced by the fact that the regeneration section can be located away from the absorption section. The sulfuric acid produced in the process should be marketable as a commercial acid. The process can be decoupled by provision of intermediate storage for spent slurry and recycle MgO between the absorption and regeneration sections. The process has good turndown ability. The process should be acceptable to the utility industry although it is more complex than some competing processes.

Suitability for Industrial Application - Comments about retrofitability, by-product marketing, and process decoupling made above, under utility acceptability apply to industrial applications as well. The process can be modularized in all sections, but the modularization of the regeneration calciner would be expensive. A similar problem would seem to limit applicability to small boilers unless a central regeneration facility were adopted. Capital requirements for a series of small local regeneration sections could be prohibitive.

Flexibility to Provide Alternate Products - The process is very well suited to produce sulfuric acid. It can also produce sulfur, but only by using a very large excess of reducing agent because the calciner off gas contains about one-half mole of O_2 per mole of SO_2. The O_2 would have to be reduced along with the SO_2 in order to produce sulfur. The 50 percent increase in reducing gas requirement to produce sulfur from SO_2 over other processes producing a concentrated SO_2 stream would probably make sulfur production economically prohibitive.

Regional/Site Considerations - The process is suitable over a broad range of applications. There appear to be no regional or site restrictions for its application.

Table 2

Magnesia Slurry-Regeneration Process

Total Capital Investment Analysis[a]

	Investment, $
Direct Investment	
Magnesium oxide and coke receiving and storage (pneumatic conveyor and blower, hoppers, conveyors, elevators, and storage silos)	308,000
Feed preparation (weigh feeders, conveyors, elevators, slurrying tank, agitator, and pumps)	381,000
Particulate scrubbers and inlet ducts (4 scrubbers including common feed plenum, effluent hold tanks, agitators, pumps, and flyash neutralization facilities)	6,222,000
Sulfur dioxide scrubbers and ducts (4 scrubbers, including mist eliminators, pumps, and exhaust gas ducts to inlet of fan)	4,090,000
Stack gas reheat (4 indirect steam reheaters)	930,000
Fans (4 fans including exhaust gas ducts and dampers between fan and stack gas plenum)	1,188,000
Slurry processing (screens, tanks, pumps, agitators, and heating coils, centrifuges, conveyors, and elevators)	1,127,000
Drying (fluid bed dryer, fans, combustion chamber, dust collectors, conveyors, elevators, and $MgSO_3$ storage silo)	1,997,000
Calcining (fluid bed calciner, fans, weigh feeders, conveyors, elevators, waste heat boiler, dust collectors, and recycle MgO storage silo)	2,260,000
Sulfuric acid plant (complete contact unit for sulfuric acid production including dry gas purification system)	6,315,000
Sulfuric acid storage (storage and shipping facilities for 30 days production of H_2SO_4)	435,000
Subtotal	25,253,000
Services, utilities, and miscellaneous	1,515,000
Total direct investment	26,768,000
Indirect Investment	
Engineering design and supervision	2,214,000
Architect and engineering contractor	554,000
Construction expense	3,827,000
Contractor's fees	1,168,000
Total indirect investment	7,763,000
Contingency	6,906,000
Total fixed investment	41,437,000
Other Capital Charges	
Allowance for startup and modifications	4,144,000
Interest during construction	4,972,000
. Total depreciable investment	50,553,000
Land	27,000
Working capital	1,344,000
Total capital investment	51,924,000

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a. Basis:

New 500-Mw coal-fired power unit (30-yr life).

Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).

Coal properties: 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu/lb.

Stack gas reheat to 175°F by indirect steam reheat.

Investment requirements for disposal of fly ash excluded.

90% SO_2 removal.

Table 3
Magnesia Slurry-Regeneration Process

Total Annual Revenue Requirements-Regulated Utility Economics[a]

	Annual quantity	Unit cost, $	Total annual amount, $
Direct Costs			
Raw material			
Lime (1st stage neutralization)	6,300 tons	48.00/ton	302,400
Magnesium oxide (98%)	1,130 tons	250.00/ton	282,500
Coke	775 tons	32.00/ton	24,800
Catalyst	1,875 liters	2.50/liter	4,700
Total raw material costs			614,400
Conversion costs			
Operating labor and supervision	39,200 man-hr	12.50/man-hr	490,000
Utilities			
Fuel oil (No.6)	5,570,200 gal	0.40/gal	2,228,100
Steam	311,000 MM Btu	2.00/M lb	622,000
Heat credit	20,300 MM Btu	-1.25/MM Btu	(25,400)
Process water	2,207,500 M gal	0.06/M gal	132,500
Electricity	72,596,000 kwh	0.029/kwh	2,105,300
Maintenance, 7% of total direct investment			1,873,800
Analyses	8,500 man-hr	17.00/man-hr	144,500
Total conversion costs			7,570,800
Total direct costs			8,185,200
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6% of total depreciable investment			3,033,200
Average cost of capital and taxes at 8.6% of total capital investment			4,465,500
Overhead			
Plant, 50% of conversion costs less utilities			1,254,200
Administrative, 10% of operating labor			49,000
Marketing 10% of sales revenue			230,000
Total indirect costs			9,031,900
Gross annual revenue requirements			17,217,100
Byproduct Sales Revenue			
Sulfuric acid	115,000 tons	20.00/ton	(2,300,000)
Total annual revenue requirements			$14,917,100

	Dollars/ton coal burned	Mills/kwh	Cents/million Btu heat input
Equivalent unit revenue requirement	9.94	4.26	47.4

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a. **Basis:**
New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up).
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned: 1,500,100 tons/yr, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Total capital investment, $51,924,000; total depreciable investment, $50,553,000,
Total direct investment, $26,768,000.
Investment and revenue requirements for disposal of fly ash excluded.
90% SO_2 removal.

PROCESS ALTERNATIVES

Direct production of elemental sulfur from $MgSO_3$ in the calciner would be very desirable since the regeneration of MgO and production of sulfur could be attained in the same vessel. This would reduce equipment requirements and provide an alternative to the production of sulfuric acid.

A study has been performed to determine the thermodynamic feasibility of $MgSO_3$ decomposition with reducing gas and conceptual designs of possible process arrangements have been performed. The results of this study show that producing sulfur in the calciner could be done either catalytically or noncatalytically. The catalytic case could use a H_2/CO reducing gas from an air blown gasifier. The noncatalytic case would probably require an H_2/CO reducing gas from an oxygen blown gasifier because of the higher temperature requirements for noncatalytic operations. The gas leaving the calciner would contain sulfur mainly in the form of elemental sulfur, H_2S, and SO_2. The gas would be cooled to condense out the elemental sulfur. The gas would then be sent to catalytic converters to react the H_2S and SO_2 together to form sulfur by the Claus reaction. The gas stream would again be cooled to condense out sulfur and then be sent to the boiler or incinerated and routed back to the SO_2 absorber.

Since the feasibility study has shown that it is thermodynamically possible to produce sulfur in the calciner, the next step would be to perform bench and pilot scale testing of the concept. This would help determine if the kinetics of the reducing gas/SO_2 reactions were favorable and would identify potential equipment design problems with the process.

SUMMARY

The magnesia slurry scrubbing process is commercially demonstrated in both Japan and the U.S. The NIIOGAAZ Process and the Grillo Process have both been tested at the pilot plant level. Advantages of the processes include minor disposal problems, reduced raw materials, minor plugging and scaling problems in the scrubber, and no reported problems with oxidation. Process disadvantages are production of a relatively dilute SO_2 stream (15%) and the need for fuel oil for absorbent regeneration. The NIIOGAAZ Process is very similar to the magnesia slurry scrubbing process developed in the U.S. No additional advantages or disadvantages for the Russian process are apparent. The Grillo Process is also similar to the U.S. Process except that manganese dioxide is added to the scrubbing slurry. It is claimed that the MnO_2 increases the SO_2 absorption rate and prevents loss of MgO activity by sintering in the calciner. Disadvantages of the Grillo Process relative to the MgO process are increased chemical complexity due to the MnO_2 addition, probable increased costs, and potential for toxic manganese compounds being formed and released to the environment.

Although the magnesia slurry process is commercial in development, several opportunities for RD&D efforts remain. Thus far, process operations have been directed more toward getting the process to run after being built rather than developing the basic chemical and kinetic data which aid in thoroughly understanding a process. Areas of further investigation are:

- studies of the rates of dissolution of recycled MgO and $Mg(OH)_2$ as functions of the type of hydrate $MgSO_3$ crystals formed,
- studies in control of calciner operating control such that dead burning is minimized,
- investigation of the kinetics of precipitation of the two types of hydrates and the supersaturation required for nucleation,
- bench scale testing and kinetic studies of direct production of sulfur in the calciner,
- evaluation of the use of power plant flue gas for drying the $MgSO_3/SO_4$ crystals,
- testing of coal as the calciner fuel in place of fuel oil which would require major equipment modifications.

References - AN-056, CA-327, DO-015, EN-316, HY-009, KO-111, KO-174, MC-076, MC-136; RA-123; RA-137

MELAMINE SLURRY SCRUBBING PROCESS

The Melamine Slurry Scrubbing Process, developed by TVA, uses a melamine slurry to absorb SO_2 followed by a thermal regeneration step. Flue gas is first treated in a venturi prescrubber to remove fly ash and chlorides. The gas is then scrubbed by the melamine ($C_3H_6N_6$) slurry in a two-stage countercurrent spray tower. One hold tank is used for each stage. The sulfite/sulfate slurry is filtered, with the liquor returning to a reslurry/recycle tank and the solids being fed to a two-stage fluid bed dryer. The first stage, which is operated at 215°F, removes free water and water of hydration. The second stage, operating at 392°F, thermally decomposes the sulfite solids to regenerate melamine and produce an SO_2-rich off-gas. Water is condensed out of the gas before it is sent to an acid plant. The regenerated melamine solids which contain some melamine sulfate, are split into two streams with two-thirds returning to the reslurry/recycle tank and one-third going to a chemical decomposition step for control of melamine sulfate. This is necessary because melamine sulfate is not decomposed in the fluid bed dryer. In this step melamine sulfate is reacted with ammonium hydroxide in a solution to precipitate melamine solids and form soluble ammonium sulfate. The solids are filtered and recycled back to the process and the ammonium sulfate is recovered as a by-product. Paraphenylenediamine, an antioxidant, is added to the process for sulfite oxidation control, limiting oxidation to about 3 percent of the absorbed SO_2. Simplified process flow diagram is presented in Figure 1.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - It is reported that the process can remove greater than 99 percent of the inlet SO_2 in the flue gas.

Multipollutant Control - The process has no multipollutant removal capability.

Secondary Pollution Problems; Air - The loss of melamine compounds in the flue gas exiting the stack could be a pollution problem. There is no reported information on melamine concentrations in the exiting flue gas. Some ammonium compounds will be recycled to the process from the sulfate decomposer since the melamine solids cannot reasonably be completely dewatered. Loss of these compounds with the exiting flue gas from the scrubber is also a potential pollution problem. Fugitive dust from the handling and transfer of dry melamine dompounds may contribute to secondary air pollution.

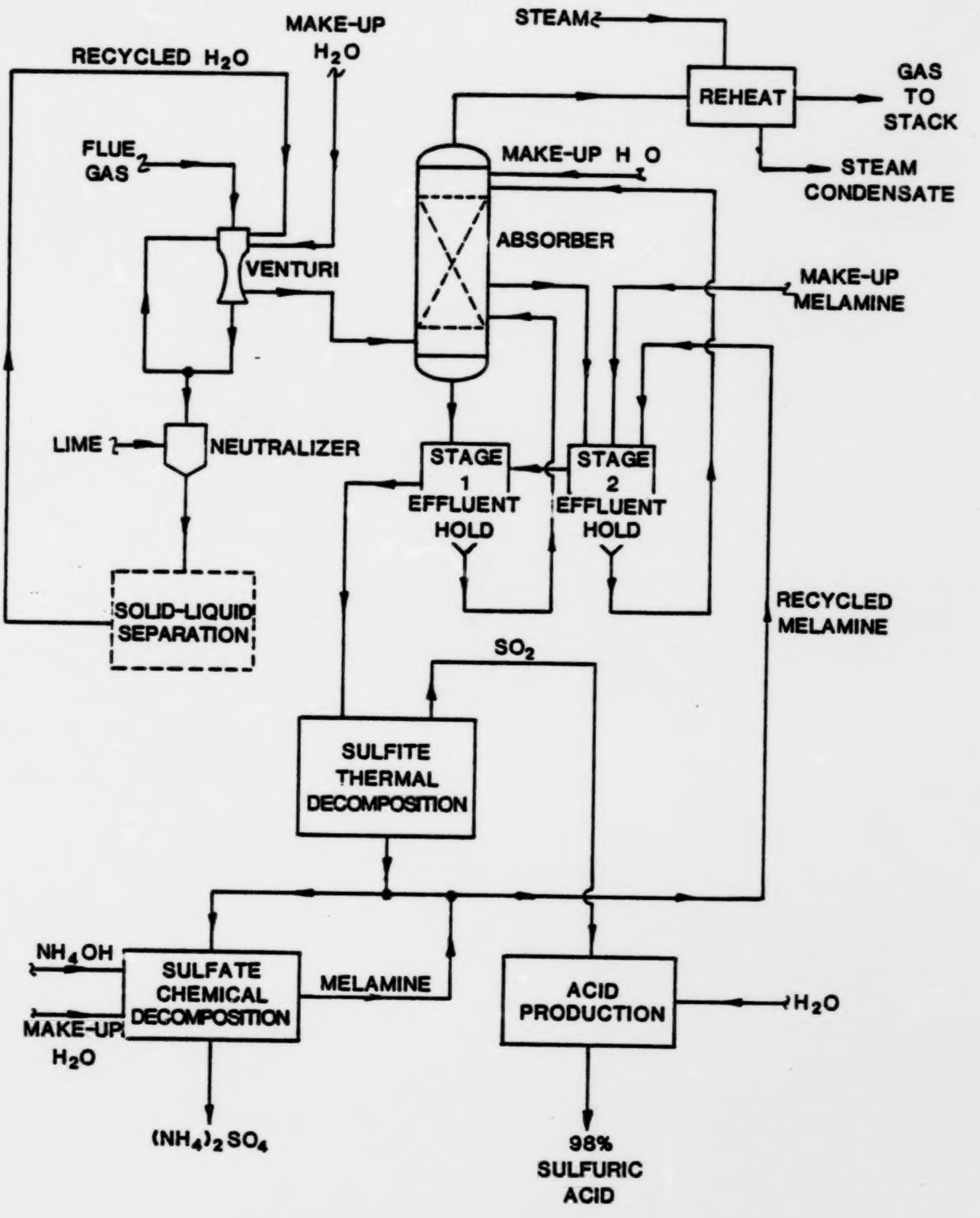
STEAM
REHEAT
GAS TO STACK
STEAM CONDENSATE
RECYCLED H_2O
MAKE-UP H_2O
FLUE GAS
VENTURI
MAKE-UP H O
ABSORBER
MAKE-UP MELAMINE
LIME
NEUTRALIZER
STAGE 1 EFFLUENT HOLD
STAGE 2 EFFLUENT HOLD
SOLID-LIQUID SEPARATION
RECYCLED MELAMINE
SO_2
SULFITE THERMAL DECOMPOSITION
NH_4OH
MAKE-UP H_2O
SULFATE CHEMICAL DECOMPOSITION
MELAMINE
ACID PRODUCTION
H_2O
$(NH_4)_2SO_4$
98% SULFURIC ACID

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR MELAMINE WET SCRUBBING PROCESS

Secondary Pollution Problems; Water - A purge stream from the process will probably need to be treated for removal of impurities introduced with makeup water, fly ash entering the absorber, and other sources. Purge requirements would be site specific and would depend on factors such as melamine makeup quality, ammonium hydroxide quality, makeup water quality, and the quantity and quality of ash which enters the system. The possibility exists of melamine decomposing into inactive chemicals as they are continually recycled in the process. The amount of testing done with recycled melamine by the process developer is unknown. If the melamine does decompose to a certain extent into useless by-products, the slurry purge stream will also need to be of an adequate volume to keep the concentrations of these chemicals at a reasonable level.

Secondary Pollution Problems; Solid - No secondary solid pollution problems are anticipated with the melamine process.

Energy Intensiveness - This process is relatively energy intensive in that it has a thermal regeneration step requiring about 90 x 10^6 Btu/hr of heat for drying and decomposing the spent melamine sulfite slurry. The current design of this process uses No. 6 fuel oil to supply heat for this step. The potential exists for using coal as a fuel for the two-stage dryer if the coal ash could be readily separated from the recycle melamine product. The process also requires stack gas reheat and steam for the ammonium sulfate crystallizer heater. The total fuel oil and steam energy requirement for the process is only slightly less than the total for the magnesia slurry scrubbing process. Raw material and energy requirements for this process are presented in Table 1.

DEVELOPMENT STATUS

Overall Status - The process has been operated on the bench scale by TVA in glassware tests. A coal-fired source was used for the flue gas, but all of the process steps were not integrated. The scale-up capability of the process is questionable at this time due to the limited development status.

Use of Commercialized Technology - The process uses current technology except possibly for the fluid bed dryer.

Process Controllability - The process is relatively complex mechanically, and is very similar in design to the magnesia slurry absorption process with the addition of a separate sulfate decomposition step. Controllability should be similar to that for the magnesia process.

TABLE 1. RAW MATERIAL AND ENERGY REQUIREMENTS FOR A MELAMINE SLURRY SCRUBBING SYSTEM

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (Dry)

		Quantity
Raw Materials		
Ammonia	(lb/hr)	340
Lime	(lb/hr)	1800
Melamine	(lb/hr)	507
Paraphenylenediamine	(lb/hr)	23
Utilities		
Process Water	(10^3 gal/hr)	525
No. 6 Fuel Oil	(10^6 Btu/hr)	90
Electricity	(Kw)	9634
Steam (500 psig)	(10^6 Btu/hr)	66.3

ECONOMIC AND TECHNOLOGICAL FACTORS

Analysis of the melamine slurry scrubbing process indicated total capital costs of \$58,195,000. Operating costs were estimated as \$10,489,000 less \$2,428,000 for sulfuric acid and ammonium sulfate by-product sales. Unit revenue requirements were estimated at 5.19 mills/kwh using a utility financing method. The processing technology is well developed except perhaps for the fluid bed dryer. But, the early stage of development of the process makes process costs somewhat uncertain since future process modification could result as the process is developed. The two-stage drying step has been costed as fuel oil-fired. Coal-firing could reduce these operating costs, but the additional capital costs would at least partially offset this advantage. A summary of capital and operating costs for the melamine slurry scrubbing process is presented in Tables 2 and 3.

APPLICABILITY

Suitability for Utility Application - The regeneration section can be located away from the absorption section so that retrofit should be possible. The sulfuric acid produced in the process should be commercial grade 98% sulfuric acid. Decoupling or centralized regeneration is possible by providing intermediate storage between the hold tank and the dryers for spent slurry and recycle melamine. The process has good turndown ability. Although the process is more complex than some competing processes, it should be acceptable to the utility industry.

Suitability for Industrial Application - Comments about retrofitability, by-product marketing, and process decoupling made above under utility application, apply to industrial applications as well. The process can be modularized in all sections, but modularization of the regeneration section would be expensive. For this reason, a centralized regeneration facility for a series of small local boiler applications would appear to be most economical.

Flexibility to Provide Alternate Products - This process produces an SO_2-rich gas stream which is very well suited to produce sulfuric acid. It can slso produce sulfur, but only by using a very large excess of reducing agent because the dryer off-gas contains about one-half mole of O_2 per mole of SO_2 . The O_2 would have to be reduced along with the SO_2 in order to produce sulfur. The 50 percent increase in reducing gas requirement to produce sulfur from SO_2 over other processes producing a concentrated SO_2 stream would probably make sulfur production economically unattractive.

Table 2

Melamine Slurry-Regeneration

Total Capital Investment Analysis[a]

Direct Investment	Investment, $
Raw materials handling	1,300,000
Feed preparation	400,000
Flue gas handling	4,800,000
Flue gas preparation	3,600,000
SO_2 absorption	4,500,000
Reheat	1,000,000
Sulfite thermal decomposition	4,400,000
Sulfuric acid production	6,100,000
Sulfuric acid storage	400,000
Sulfate chemical decomposition	260,000
Ammonium sulfate removal	1,760,000
Subtotal	28,520,000
Services	1,710,000
Total direct investment	30,230,000
Indirect Investment	
Engineering design and supervision	2,100,000
Architect/engineering contractor	525,000
Construction expense	4,235,000
Contractor fees	1,280,000
Total indirect investment	8,140,000
Contingency	7,670,000
Total fixed investment	46,040,000
Other Capital Charges	
Allowance for startup and modifications	4,605,000
Interest during construction	5,525,000
Total depreciable investment	56,170,000
Land	25,000
Working capital	2,000,000
Total capital investment	58,195,000

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[a] Basis:
New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).
Coal properties; 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Investment requirements for disposal of fly ash excluded.
90% SO_2 removal.

Table 3
Melamine Slurry Scrubbing Process

Total Annual Revenue Requirements-Regulated Utility Economics[a]

Direct Cost	Annual quantity	Unit cost, $	Total annual amount, $
Raw materials			
Lime (First stage neutralization)	6,300 tons	48.00/ton	302,000
Melamine	1,775 tons	940.00/ton	1,668,000
Ammonia	1,190 tons	200.00/ton	238,000
Paraphenylenediamine	162,000 lb	4.04/lb	650,000
Total raw material costs			2,858,000
Conversion			
Operating labor and supervision	49,000 man-hr	12.50/man-hr	612,000
Utilities			
Fuel Oil (No. 6)	4,200,000 gal	0.40/gal	1,680,000
Steam	464,000 MM Btu	2.00/M lb	928,000
Process water	3,672,000 MM Btu	0.06/M gal	220,000
Electricity	67,438,000 kwh	0.029/kwh	1,956,000
Maintenance, 7% of total direct investment			2,116,000
Analyses	7,000 man-hr	17.00/man-hr	119,000
Total conversion costs			7,631,000
Total direct costs			10,489,000
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6% of total depreciable investment			3,370,000
Average cost of capital and taxes at 8.6% of total capital investment			5,005,000
Overhead			
Plant, 50% of conversion costs less utilities			1,424,000
Administrative, 10% of operating labor			61,000
Marketing 10% of sales revenue			243,000
Total indirect costs			10,103,000
Gross annual revenue requirements			20,592,000
By-Product Sales Revenue			
Sulfuric acid	111,000 tons	20.00/ton	2,220,000
Ammonium sulfate	4,620 tons	45.00/ton	208,000
Total by-product sales revenue			2,428,000
Total annual revenue requirements			18,164,000

	Dollars/ton coal burned	Mills/kwh	Cents/million Btu heat input
Equivalent unit revenue requirement	12.10	5.19	57.7

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a. Basis:

New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up).
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned: 1,500,100 tons/yr, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Total capital investment, $58,195,000; total depreciable investment, $156,170,000; total direct investment, $30,230,000.
Investment and revenue requirements for disposal of fly ash excluded.
90% SO_2 removal.

Regional/Site Considerations - The process should be suitable over a broad range of applications. There appears to be no regional or site restrictions for its application.

SUMMARY

The melamine slurry scrubbing process has been tested on the bench scale by TVA, but without integration of all process steps. Advantages of the process include minor disposal problems, low temperature regeneration, and reduced fuel oil requirements over the MgO scrubbing process which is comparable in design. Process disadvantages are production of a relatively dilute SO_2 stream (15%), the need for fuel oil for melamine regeneration, and the need for a separate step for sulfate decomposition. The major process problem is its early development status.

References - MC-322

RESOX SUBSYSTEM

The RESOX process is a subsystem for direct conversion of SO_2 in regenerator off gas to elemental sulfur through the use of coal as a reductant. A process flow diagram is presented in Figure 1. SO_2 rich gas is routed to a reactor where it is countercurrently contacted with a stream of crushed anthracite coal. Steam and air are also injected into the reactor with the overall reaction:

$$C + SO_2 \rightarrow CO_2 + S \qquad (1)$$

The gas stream exits the reactor and passes to an inclined shell and tube condenser where sulfur is condensed on the tube side and steam is generated on the shell side. Part of this gas stream, which contains residual SO_2, is recycled to the FGD system so that further SO_2 removal can be achieved. Molten sulfur is removed from the condenser and sent to sulfur storage or sales.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Conversion - The RESOX process generally achieves 90-95 percent conversion of the inlet SO_2 to elemental sulfur. However, since the off gases are recycled to the SO_2 removal system, SO_2 conversion for the integrated system can be 99+ percent.

Potential for Multipollutant Removal - The process seems to have little potential for removal of pollutants other than SO_2 from the entering stream.

Secondary Pollution Problems; Air - Recycle of off gases to the sulfur removal system could result in buildup of carbon-sulfur compounds (COS, CS_2, etc.) and subsequent release to the atmosphere. Recycle of off gases to the boiler could solve this potential problem.

Secondary Pollution Problems; Water - No secondary water pollution problems are anticipated with the RESOX process. Boiler blowdown from the sulfur condenser can be treated in the plant water system.

Secondary Pollution Problems; Solid - Anthracite residue contains ash and unused carbon which can be disposed of by the plant ash disposal system. It may be desirable, however, to place it in the boiler for combustion. Sulfur produced from the process will likely contain some hydrocarbon, trace element, and particulate contamination. These may make the sulfur unsuitable for general use and restrict it to such uses as fertilizer manufacture. Demonstration plant operation with coals other than anthracite should clear up this point.

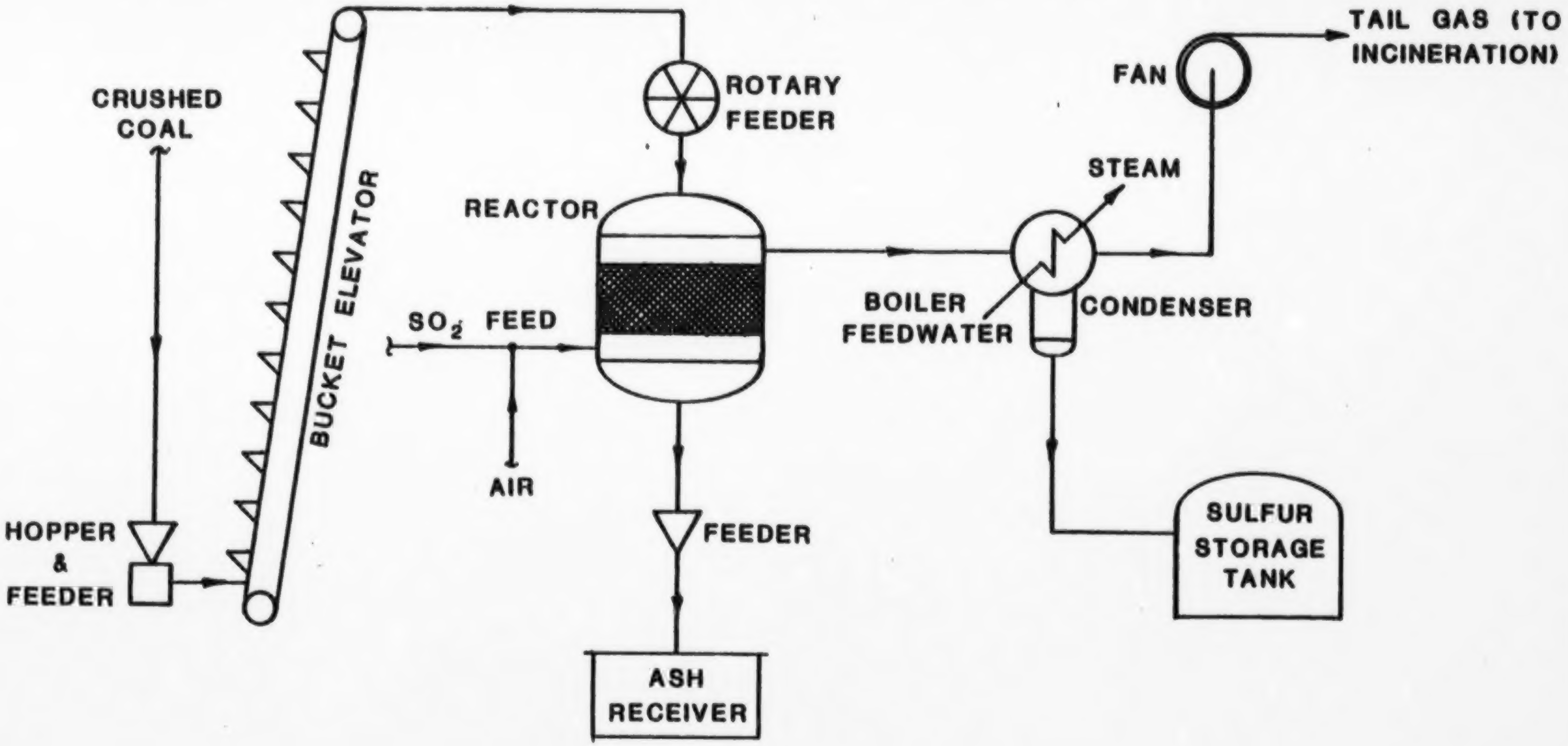
CRUSHED COAL
HOPPER & FEEDER
BUCKET ELEVATOR
ROTARY FEEDER
REACTOR
SO_2 FEED
AIR
FEEDER
ASH RECEIVER
BOILER FEEDWATER
STEAM
CONDENSER
FAN
TAIL GAS (TO INCINERATION)
SULFUR STORAGE TANK

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR RESOX PROCESS

Energy Intensiveness - Major energy uses in the RESOX system include electricity for a fan to supply power for tail gas movement, pumps for the molten sulfur and coal for reduction of the SO_2. Coal usage could be relatively high if the unreacted char were disposed of with the ash since only about 50 percent carbon utilization is achieved. Overall, the process is not a large energy consumer, mainly because the major energy source is raw coal and not a higher energy form such as reducing gas.

Raw material and utility requirements for the process are presented in Table 1.

TABLE 1. RAW MATERIAL AND UTILITY REQUIREMENTS FOR RESOX SUBSYSTEM

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (Dry)

Raw Materials		
Anthracite Coal	Tons/hr	5.6
Utilities		
Electricity	kw	500

The major raw material for the RESOX process is coal. In addition, steam is injected to control process temperatures when necessary. However, this steam is intermittent and not required under stable operating conditions. Thus, it is not included. The process also produces 50 psig steam from the sulfur condensation unit. This steam is used for tracing of sulfur lines and maintenance of the sulfur in its molten state and is thus not claimed as a credit to the process. Utilities include electricity for fans and pumps.

Solid waste disposal from the process is not listed under utility services. It appears that the best method for dealing with this problem may be to recycle the ash and unreacted carbon to the boiler where the residual ash would be disposed of in the plant ash disposal system.

DEVELOPMENT STATUS

Overall Development - Development of the RESOX process was begun by Foster-Wheeler in the late 1960's. The process has been demonstrated at the 20 Mw level in an integrated Bergbau-Forschung/Foster Wheeler unit. The process was started up in 1975 at Gulf Power Company's Scholz Steam Plant. The system has been operated with fairly encouraging results. A full scale demonstration unit for testing of the integrated system is underway in Germany at this time, under sponsorship of EPRI and others. The RESOX process is moving to the demonstration stage. Major problems are 1) particulate plugging of the sulfur condenser, 2) controlling the reaction system, and 3) using a substitute for anthracite coal (discussed further in process alternatives). Sulfur quality is a potential problem that needs to be resolved before the process can be commercialized. In addition, the process has been investigated only for a limited number of feed gas compositions and further investigation is necessary to determine the effects of various feed gas compositions on the process.

Use of Commercialized Technology - The key piece of equipment in the process, the reactor, is not commercial. This unit is complex and remains to be demonstrated on a large scale. Remaining equipment in the process uses commercial technology.

Process Controllability - Control of the RESOX process can be expected to be moderately difficult due to limitations on reactor operating conditions. If the temperature rises too high, excessive H_2S will be formed. If the temperature is too low, sufficient residence time for SO_2 conversion is not allowed. This necessary reactor temperature control is generally accomplished with steam injection. In addition, the exact optimum temperature is dependent on H_2O/SO_2 ratio, other feed characteristics, and coal characteristics.

ECONOMIC AND TECHNOLOGICAL CONSIDERATIONS

The economics of the RESOX process can be regarded as tentative due to development status. Reported costs for the process reported on a 500 Mw system are in the 4-8 million dollar range. Thus capital costs seem in the same range as the Allied Reduction system. Technological factors do not seem to have much potential for reducing costs, and the problems that remain to be solved with the process could increase costs. Areas primarily referred to are particulate control in the reactor gas to the sulfur condenser, disposal of the potentially low quality sulfur from the process, and applicability of coals other than anthracite.

APPLICABILITY

Applicability of the RESOX process to flue gas desulfurization systems in general is not known at this time. It has been operated to date only with the Bergbau-Forschung process off gas and thus is unproven in other applications. There are no factors that should inhibit application of the RESOX process to off-gas from other flue gas desulfurization systems, but verification of this must be made with experimental operation.

There is some concern that the sulfur product from the process may be of low quality due to contamination with particulates and volatiles from the coal. This could hinder sulfur marketability at a specific site.

Another potential site limitation for the RESOX process is anthracite availability. It could be prohibitively expensive in those parts of the country distant from mining sites. Anthracite will probably not prove to be an adequate solution to the problem of providing coal to the process in the long term. The process may have difficulty following load in a utility service due to anticipated complexity of control. Acceptability of the process to the utility industry may be a problem due to these control characteristics.

PROCESS ALTERNATIVES

There are two process alternatives that should be examined before the process is commercialized. These are use of coals other than anthracite and recycle of off gas to the boiler.

Use of Other Coals - Use of the same coal as that being burned in the boiler would seem to be a good solution to problems of anthracite availability and handling of two separate coal supplies. A problem inherent in such a system is the high volatiles content of many coals. Volatile hydrocarbons will vaporize in the top of the RESOX reactor and be removed from the system in the off gas before they have a chance to react to a significant extent. These volatiles will potentially reduce the value of the product sulfur and cause buildup and eventual discharge to the atmosphere of such pollutants as COS and CS_2. These problems could be reduced in two areas. One method is to devolatilize the coal before it enters the reactor. The hydrocarbon gases could then be routed to the boiler for combustion or condensed and sold. A second method would be to find a market for low quality sulfur and route the RESOX tail gas to the boiler for combustion of residual hydrocarbons.

Recycle to Boiler - When using a coal other than anthracite, the RESOX tail gas would probably have to be recycled to the boiler. The volatile hydrocarbons present in the stream could increase the concentrations of carbonyl sulfide and carbon disulfide to unacceptable levels. Recycle of this stream to the boiler would seem to be a potential solution to this problem.

SUMMARY

The RESOX process seems to have potential for solving one of the most difficult problems in Flue Gas Desulfurization, conversion of SO_2 directly to sulfur without the use of a reducing gas.

The process is, however, undeveloped and would seem to be an excellent candidate for future support. Major problems that must be resolved, in addition to problems of overall technology, are the suitability of lower rank coals than anthracite and the utilization of sulfur that is potentially contaminated with particulate matter and condensed hydrocarbons.

Another problem that could be worthy of further support is the applicability of the RESOX process to processes other than the Bergbau-Forschung process. There is as yet no data on the process in other services and it should prove more widely applicable than to just the Bergbau-Forschung process.

References - BI-031, BI-072, HA-352, ST-292, ST-369.

SHELL/UOP COPPER OXIDE PROCESS

The Shell/UOP Copper Oxide Process uses the concept of adsorption and reaction of SO_2 with copper oxide and oxygen to form $CuSO_4$. Regeneration of copper oxide is accomplished through the use of a hydrogen reducing gas. A concentrated SO_2 stream is produced which is suitable for sulfur or sulfuric acid production.

Hot flue gas is routed through a hot electrostatic precipitator (750°F) for particulate removal. The hot gas is then contacted with copper oxide on an alumina acceptor in a fixed bed reactor. In the reactor, reaction 1 occurs and the SO_2 is removed from the flue gas.

$$CuO + SO_2 + \tfrac{1}{2}O_2 \rightarrow CuSO_4 \tag{1}$$

The flue gas is then routed through an air heater and economizer, and to the stack. When the copper oxide has been largely converted to $CuSO_4$, the bed is switched off stream for the regeneration step (multiple beds provide continuous SO_2 removal).

Regeneration of copper oxide is achieved through reaction of $CuSO_4$ with a hydrogen reducing gas. The reducing gas can be produced by any of a number of methods, with steam naphtha reforming being the method addressed in the economic analysis of the process. In this system, reducing gas regenerates copper by reaction 2.

$$CuSO_4 + 2H_2 \rightarrow Cu + SO_2 + 2H_2O \tag{2}$$

At this point, a number of options are available for separation of the water and SO_2 and are discussed further under process alternatives. The process as addressed here involves quench of the hot regenerator off gas and steam stripping of the resulting water-SO_2 stream. The SO_2 rich stream from steam stripping is further concentrated by compression and condensation of the water, which is then recycled to the quench system or to disposal.

The rich SO_2 stream is then fed to a modified Claus unit where it reacts with hydrogen to produce elemental sulfur. Options in this area are also discussed in the process alternatives section.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - SO_2 removal efficiencies of 95 percent have been reported by the process developer.

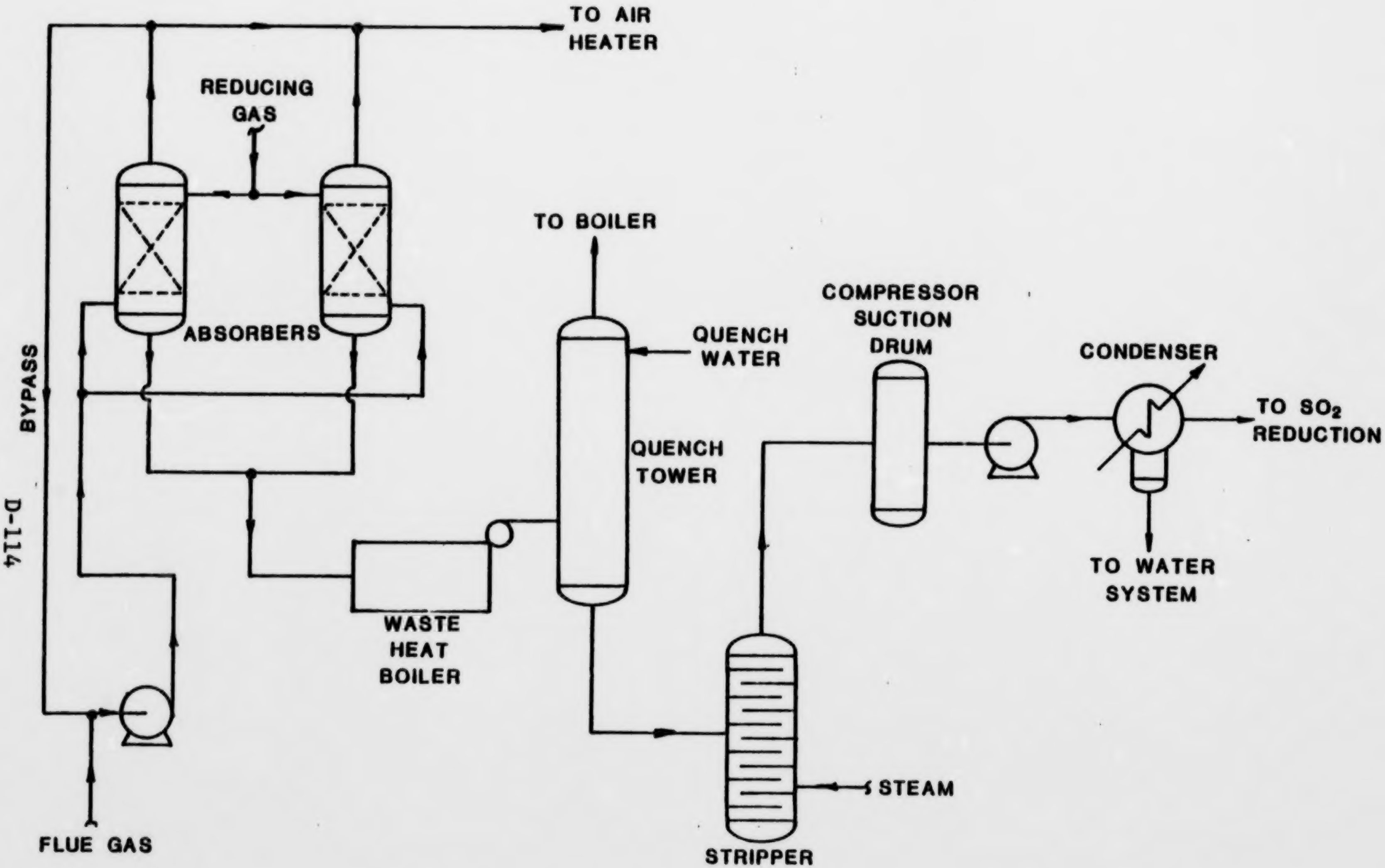
TO AIR HEATER
REDUCING GAS
ABSORBERS
BYPASS
TO BOILER
QUENCH WATER
QUENCH TOWER
WASTE HEAT BOILER
FLUE GAS
COMPRESSOR SUCTION DRUM
CONDENSER
TO SO_2 REDUCTION
TO WATER SYSTEM
STEAM
STRIPPER

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR SHELL/UOP COPPER OXIDE PROCESS

Multipollutant Control - The copper oxide process will show improved particulate removal due to the requirement that a high efficiency electrostatic precipitator be used to protect the copper oxide bed. The process can also achieve up to 80 percent NO_x reduction through the addition of one mole of ammonia per mole of NO_x. Shell has recommended a design for 75 percent NO_x removal.

Secondary Pollution Problems: Air - In installations where ammonia is injected for NO_x control, the potential for secondary emissions of ammonia exists. This problem should be relatively easy to control through careful operation under design conditions. However, the problem would seem to limit potential for NO_x removal to 75 to 80 percent.

Secondary Pollution Problems; Water - Water is produced in the regeneration section and added at various points in the system such that excess water with 30 to 50 ppm of dissolved SO_2 is produced. It could also contain quantities of trace elements if used in coal-fired applications. Disposal or treatment of this water could present problems.

Secondary Pollution Problems; Solid - Disposal of attritted copper oxide acceptor has some potential for secondary pollution. This should not be a serious problem.

Energy Intensiveness - The copper oxide process is a fairly energy intensive process due to its stoichiometric requirement for hydrogen of two moles hydrogen per mole of inlet sulfur dioxide in the regeneration step. If sulfur is produced in the process (as addressed in this analysis) a total of 4 moles hydrogen per mole of inlet SO_2 is required. Data indicate that the stoichiometric hydrogen requirements would be exceeded and actual consumption would be 5.5-6.1 moles H_2/mole SO_2. A summary of raw material and energy requirements is presented in Table 1.

Heat credits in the table below are vendor estimates of net energy credited to the process from fan compression, combustion of reducing gas, plus other credits. As such, they are somewhat higher than those for other processes evaluated, but their effect upon overall costs is negligible. Reduction of this heat credit by one half would increase annual costs by only 3.6 percent to value of 9.6 mills/kwh.

TABLE 1. RAW MATERIAL AND UTILITY REQUIREMENTS FOR SHELL/UOP COPPER OXIDE PROCESS

Basis: 500 Mw system, 90% SO_2 Removal, 3.5% Sulfur Coal (Dry)

Raw Materials		
Naphtha (H_2 production)	(gal/hr)	2,479
Utilities		
Naphtha (fuel)	(gal/hr)	620
Process Water	(gal/hr)	900
Electricity	(kw)	8,914
Heat Credit	(MM Btu/hr)	286

DEVELOPMENT STATUS

Overall Status - Shell has tested the process at its Pernis refinery in some 20,000 hours of operating time to test acceptor characteristics, reactor construction materials, and regeneration agents. Scale-up was made in 1973 to a 40 Mw equivalent unit at the SYS refinery in Japan. This was not an integrated unit due to the refinery's excess supply of hydrogen and Claus plant capacity.

The system is presently being operated on a 0.6 Mw unit at Tampa Electric's Big Bend Station to evaluate long-term catalyst activity and pressure drop. The availability of design information is good, but a fully integrated system to answer questions about system reliability and load following ability is needed.

Use of Commercialized Technology - The major process area requiring non-commercial technology is in the switching valves required to bring the reactors on and off line. These valves have been a source of trouble in previous operation and need to be demonstrated in long term operation. The process has not yet been operated as an integrated unit and such operation is necessary in order for the process to be considered commercial. The copper oxide beds and other process technology can be regarded as commercial.

Process Controllability - Control of the process is a key issue in its overall cost. In order to maximize cycle time and keep hydrogen usage to a minimum, it is necessary to switch the bed to a recycle mode on the basis of SO_2 breakthrough instead of a time schedule. This is due to the fact that unreacted copper oxide requires a mole of hydrogen in the regeneration section. Another problem with the process is integration of the swing mode adsorption/regeneration into a continuous chemical process for sulfur work-up. This could be a difficult problem in the area of process control.

ECONOMIC AND TECHNOLOGICAL FACTORS

Estimates of the costs associated with the copper oxide process are presented in Tables 2 and 3. Total capital costs for the process were estimated at approximately $95 million. Annual direct costs were estimated at $13 million and annual revenue requirements at $27 million. The resulting unit cost is estimated at 7.67 mills/kwh based upon utility financing.

The costs associated with the Shell/UOP Copper Oxide Process appear to be relatively sensitive to technological factors in two areas. One area is the area of hydrogen production and consumption. Consumption of hydrogen is much higher than stoichiometric and reduction would be beneficial. Production of hydrogen from a less expensive source could also cut costs. This alternative is discussed in the process alternatives section. An area of potential cost escalation is the switching valves for changing the reactor from acceptance to regeneration mode. Although some progress has been made in design of these valves, short lifetimes and more expensive valves could contribute to increased process costs at time of commercialization.

The Shell/UOP Process has been estimated to have relatively high in capital cost. This is due largely to the mechanical complexity of the process, high hydrogen requirements, and requirement for high temperature electrostatic precipitation.

APPLICABILITY

Suitability for Utility Application - The Shell/UOP Process cannot be easily retrofitted due to its requirement that flue gas be contacted at high temperature with the acceptor. Retrofit would require extensive ductwork or reheat of the flue gas to 700°F. The process is capable of producing sulfur, sulfuric acid or liquid SO_2 depending upon the method chosen. The process could be decoupled through the use of excess beds and storage of SO_2 in the bed until regeneration is desired. However, this would likely be expensive and undesirable from a process standpoint. The process can follow load if a bypass system is provided for recycle of treated gas to the acceptor reactor inlet to maintain adequate space velocity. Turndown of the system is limited to 60-70 percent unless such a recycle system or a series of smaller reactors is employed.

Table 2

Universal Oil Products Company-SFGD Process

Total Capital Investment Analysis[a]

	Investment, $
Direct Investment	
Electrostatic precipitators (4 high temperature electrostatic precipitators)	14,893,000
Sulfur dioxide reactors (6 reactors, waste heat boiler, blowers, bypass ducts, exhaust gas ducts and dampers)	18,542,000
Sulfur dioxide workup (quench tower, stripper, gas holding drum, gas compressor, pumps, filters)	4,239,000
Modified Claus (reduction burner, reactors, steam generators, sulfur coalescer, incinerator, sulfur storage pit, line burners, blowers, pumps)	3,441,000
Steam-naphtha reformer	8,274,000
Subtotal	49,389,000
Services, utilities, and miscellaneous	2,963,000
Total direct investment	52,352,000
Indirect Investment	
Engineering design and supervision	1,967,000
Architect and engineering contractor	492,000
Construction expense	6,678,000
Contractor's fees	1,944,000
Total indirect investment	11,081,000
Contingency	12,687,000
Total fixed investment	76,120,000
Other Capital Charges	
Allowance for startup and modifications	7,612,000
Interest during construction	9,134,000
Total depreciable investment	92,866,000
Land	18,000
Working capital	2,488,000
Total capital investment	95,372,000

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[a] Basis:

New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).
Coal properties: 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu/lb.
Investment requirements for disposal of fly ash excluded.
90% SO_2 removal.

Table 3
Universal Oil Products Company-SFGD Process
Total Annual Revenue Requirements Analysis[a]

	Annual quantity	Unit cost, $	Total annual amount, $
Directs Costs			
Delivered raw materials			
Naphtha	17,358,000 gal	0.50/gal	8,679,000
Catalyst (modified Claus)			97,200
Catalyst (steam/naphtha reformer)			162,000
Subtotal raw materials cost			8,938,200
Conversion costs			
Operating labor and supervision	35,000 man-hr	12.50/man-hr	437,500
Utilities			
Naphtha	4,339,000 gal	0.50/gal	2,169,500
Heat credit	2,003,000 MM Btu	-1.25/MM Btu	(2,503,800)
Process water	6,300 M gal	0.12/M gal	800
Electricity	62,403,000 kwh	0.029/kwh	1,809,700
Maintenance, 4% of direct investment			2,094,100
Analyses	9,160 man-hr	17.00/man-hr	155,700
Subtotal conversion costs			4,163,500
Subtotal direct costs			13,101,700
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6% of total depreciable investment			5,572,000
Average cost of capital and taxes at 8.6% of total capital investment			8,202,000
Overhead			
Plant, 50% of conversion costs less utilities			1,343,700
Administrative, 10% of operating labor			43,800
Marketing, 10% of sales revenue			158,900
Subtotal indirect costs			15,320,400
Gross annual revenue requirements			28,422,100
Byproduct Sales Revenue			
Sulfur	35,300 long tons	-45.00/long ton	(1,588,500)
Subtotal byproduct sales revenue			
Total annual revenue requirements			26,833,600

	Dollars/ton coal burned	Mills/kwh	Cents/million Btu heat input
Equivalent unit revenue requirement	17.89	7.67	85.2

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a. Basis:
New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up).
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned: 1,500,100 tons/yr, 10,500 Btu/lb.
Total capital investment, $95,372,000; total depreciable investment, $92,866,000; total direct investment, $52,352,000.
Investment and revenue requirements for disposal of fly ash excluded.
90% SO_2 removal.

Suitability for Industrial Application - The comments above in regard to utility application in retrofitability, by-product utilization, and separability apply to industrial suitability. The process could be modularized, but the amount of switching necessary, control problems, and expense would probably make such an approach undesirable. The process does not seem to be particularly applicable to small boilers due to the number of pieces of equipment that are required.

Flexibility to Provide Alternate Products - The Shell/UOP Copper Oxide Process can produce sulfur, sulfuric acid or liquid SO_2 depending upon the method chosen for processing the SO_2 rich stream generated in the process.

Regional/Site Considerations - The process does not appear limited in terms of site considerations in view of its ability to produce a product that most closely matches regional needs.

PROCESS ALTERNATIVES

Hydrogen Production - Due to its impact on overall process costs, the hydrogen production area is very important. The process as presented has used steam/naphtha reforming to supply hydrogen. Coal gasification, although more capital intensive than steam naphtha reforming, might provide a lower cost, but more complex alternative for hydrogen production.

SO_2 Recovery and Concentration - Three alternatives for recovery and concentration have been identified; absorption/stripping, compression and water vapor condensation, and complete liquefaction. The original method proposed by UOP was absorption/steam stripping. In such a system, the regenerator off gas is quenched, absorbed into water and then steam stripped. This appears to be the least attractive of the process alternatives because of its high steam requirements and is now used only where inexpensive steam is available.

Compression and water vapor condensation is presented in this study. This system has lower steam requirements, but increased compressor motive power energy. The resulting rich SO_2 stream can be used for sulfur or sulfuric acid manufacture. This alternative appears to be more attractive economically than absorption/steam stripping in most applications.

A final method for achieving SO_2 recovery and concentration is to further compress the stream and liquefy the SO_2. This could prove a good option in areas where a market for liquid SO_2 exists. This would also reduce costs significantly compared to molten sulfur production.

SUMMARY

The Shell/UOP Copper Oxide Process has as its principle advantages the ability to produce three potential by-products; sulfur, sulfuric acid and liquid SO_2, and its ability to remove NO_x. The process is complex and would be difficult to integrate due to its high temperature absorbers and swing mode operation. Most critically, its costs appear to be high relative to other processes. Research into an integrated unit could be beneficial. However, the process appears to have merit only if simultaneous NO_x removal must be achieved.

References - DA-030, DA-147, NA-225, PA-109, SC-341, SL-062, SL-065, SL-080, UN-030.

SODIUM CARBONATE THROWAWAY PROCESS

Sodium Throwaway Processes use either a dry sodium alkali or a wet scrubbing solution to remove SO_2 from flue gas. The wet process uses NaOH, Na_2CO_3, $NaHCO_3$, or some other sodium alkali in a wet scrubber or spray dryer for gas cleaning. The operation of the wet scrubber and spray dryer are characterized by a low L/G and a clean scrubbing liquor because of the high solubility of sodium salts. The absorption reactions which take place in the scrubber are as follows:

$$2NaOH_{(\ell)} + SO_{2\,(g)} \rightarrow Na_2SO_{3\,(\ell)} + H_2O$$

$$Na_2CO_{3\,(\ell)} + SO_{2\,(g)} \rightarrow Na_2SO_{3\,(\ell)} + CO_2$$

$$2NaHCO_{3\,(\ell)} + SO_{2\,(g)} \rightarrow Na_2SO_{3\,(\ell)} + H_2O_{(\ell)} + 2CO_{2\,(g)}$$

Oxidation to sodium sulfate also occurs to different extents depending on the application of the process.

The majority of the scrubbing liquor is recycled back to the scrubber with a small bleed stream taken off to remove Na_2SO_3/Na_2SO_4 salts. Makeup sodium alkali is added to the bleed stream in a hold tank to precipitate the Na_2SO_3/Na_2SO_4 salts. The solid waste is dewatered and sold or disposed of in an environmentally acceptable manner.

The dry process has most often used nahcolite ($NaHCO_3$) or trona ($NaHCO_3$ and Na_2CO_3) to remove SO_2 because they are cheap sources of sodium alkali. The alkali is contacted with the flue gas in one of the following ways:

- Powder reagent precoating of fabric filter bags with additional feeding of reagent into the flue gas entering the baghouse.
- Passing the flue gas through a fixed bed or a fluid bed of the reagent.
- Hot zone injection with downstream removal.

The reactions which take place in the process are as follows:

$$Na_2CO_{3\,(s)} + SO_{2\,(g)} \rightarrow Na_2SO_{3\,(s)} + CO_{2\,(g)}$$

$$2NaHCO_{3\,(s)} + SO_{2\,(g)} \rightarrow Na_2SO_{3\,(s)} + H_2O_{(g)} + 2CO_{2\,(g)}$$

$$Na_2SO_{3\,(s)} + \tfrac{1}{2}O_{2\,(g)} \rightarrow Na_2SO_{4\,(s)}$$

Almost complete oxidation to sodium sulfate occurs in the dry process. The spent material from the process is water soluble and must be properly disposed of.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - Wet scrubbing with a solution of Na_2CO_3 can achieve up to 99 percent removal of SO_2. When using a spray dryer the process can be designed to remove 90 to 95 percent of the SO_2 in the flue gas.

The removal efficiency of the dry process depends upon the temperature and the residence time between the alkali and the SO_2. The following points can be made concerning SO_2 removal for the dry process:

1) Precoating of fabric filter bags with additional feeding of alkali into the flue gas prior to the baghouse can achieve only 60 to 70 percent SO_2 removal with an alkali utilization of 50 to 60 percent.

2) The use of a countercurrent moving bed can achieve up to 95 percent SO_2 removal with an alkali utilization of better than 90 percent.

3) Hot zone injection with downstream removal can achieve 90 percent SO_2 removal with an alkali utilization of 90 percent.

Multipollutant Control - The wet processes are usually preceded by particulate collection equipment so that only a small amount of particulates are captured in the scrubber. There is no reported NO_x removal for the wet processes.

For the fabric filter and hot zone injection process the SO_2 and particulates are removed simultaneously by a fabric filter or ESP. Attainable particulate removal efficiencies for fabric filters are 99.7 percent and for ESP's 99.8 percent. The moving bed process requires that the bulk of the particulate matter be removed upstream of the absorber to prevent plugging of the bed and an excessive pressure drop across the bed. Some additional particulate removal will be achieved in the absorber.

Tests conducted to determine NO_x removal by the dry processes have been inconclusive and sometimes inconsistent. There is some evidence that nahcolite can remove up to 40 percent of the inlet NO_x; therefore, further tests are warranted.

Secondary Pollution Problems; Air - There are no secondary air pollution problems associated with the processes except for possible fugitive particulate emissions from the dry processes.

Secondary Pollution Problems; Water - Secondary water problems are associated with solids disposal since the sodium salts are highly soluble.

Secondary Pollution Problems; Solids - The most serious pollution problem with these processes is solid waste disposal. The spent material from the wet processes contains sodium sulfite, sodium sulfate, sodium carbonate, and some inerts. Disposal of this material presents a large problem because it is highly water soluble and cannot be used for landfill without further treatment.

Several disposal possibilities have been considered, but more research is required. The disposal options studied include:

- Developing a market for the resultant salt cake.
- Short term storage of the waste with eventual recovery of sodium products.
- Insolubilizing the waste by forming complex salts.
- Returning waste to mines.
- Permanent storage of waste in lined and covered pits.

The solid waste disposal problem for the dry process is only slightly less severe than for the wet process because the solids are dry and smaller in volume than for the wet process. The composition of the solid waste is different in that the sulfur is mostly in the form of sodium sulfate instead of sodium sulfite, and with the probable removal of NO_x by the dry processes, there could be sodium nitrate present.

Energy Intensiveness - Raw material and utility requirements were calculated for four cases; two cases for wet scrubbing systems and two cases for dry removal. Table 1 presents the four cases with their design bases while Table 2 presents the calculation results.

The differences between the wet systems are due to the fact that the spray dryer does not saturate the flue gas and produces a dry solid waste. Since the spray dryer does not saturate the flue gas no reheat is required and thus its energy intensiveness is much lower than for the wet scrubbing process. The spray dryer does require an ESP downstream of the dryer to remove the

TABLE 1. DESIGN BASES FOR SODIUM THROWAWAY PROCESSES

	Wet Scrubber	Spray Dryer	Fixed Bed	Fabric Filter
Stoichiometry (moles Na_2CO_3 or $NaHCO_3$/mole SO_2 sorbed)	1.05	1.2	2.22	2.66
L/G (gal/1000 scf)	10	0.3	--	--
Pressure Drop (in. H_2O)	12.5	14	21.5	9.5
Oxidation Fraction (moles sulfate formed/mole SO_2 sorbed)	0.25	0.25	.90	.90
Stack Temperature after SO_2 removal (°F)	125	175	300	300
Alkali Composition	Na_2CO_3 (99.8%)	Na_2CO_3 (99.8%)	Nahcolite (70% $NaHCO_3$)	Nahcolite (70% $NaHCO_3$)

TABLE 2. RAW MATERIAL AND UTILITY REQUIREMENTS FOR SODIUM THROWAWAY SCRUBBING SYSTEMS

Basis: 500 Mw system, 90% SO_2 Removal, 3.5% Sulfur Coal (Dry)

		Wet Scrubber	Spray Dryer	Fixed Bed	Fabric Filter[3]
Raw Materials					
Na_2CO_3	(tons/hr)	19.7	22.5	--	--
Nahcolite ($NaHCO_3$)	(tons/hr)	--	--	47.1	40.7
Utilities					
Process Water	(10^3 gal/hr)	36.0	21.0	--	--
Electricity					
Pumps	(kw)	360	20	--	--
Fan	(kw)	3020	3380	5190	2290
Nahcolite Preparation	(kw)	(1)	(1)	1320	1580
Other	(kw)	--	3920 (ESP)	--	--
Steam (500 psig)	(MM Btu/hr)	51.1	--	--	--
Solid Waste	(tons/hr)	47.8 (50% solids)	26.7	57.0	47.9

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[1] Na_2CO_3 assumed to be purchased in form suitable for SO_2 absorption

[2] 10,000 Btu/kwh, 1200 Btu fuel/lb 500 psig steam

[3] Designed for 65 percent removal efficiency

spent alkali. The ESP consumes some electricity. Also, since the spray dryer produces a dry solid waste the amount of waste material to dispose of is about one-half of the wet solids from the wet scrubbing process which are dewatered to about 50 percent solids.

The dry processes differ in SO_2 removal capability, absorbent stoichiometry, and pressure drop. The fixed bed process can achieve 90 percent SO_2 removal but the fabric filter process can achieve only about 65 percent removal at the flue gas temperature of 300°F. Also, the absorbent stoichiometry for the fabric filter is higher than for the fixed bed. For these reasons the fabric filter produces more dry solid waste than the fixed bed does for the same SO_2 removal. The fabric filter pressure drop is low and the fixed bed pressure drop is rather high so the fabric filter process consumes less electricity and is less energy intensive than the fixed bed process.

DEVELOPMENT STATUS

Overall Status - Wet scrubbing with a solution of sodium carbonate has been developed in both the U.S. and Japan. In the U.S., sodium carbonate scrubbing is commercially practiced on 375 Mw of generating power at the Nevada Power Reid Gardner station. The scrubbing system was designed based on information and data obtained from an 8000 acfm pilot plant program conducted at the station in 1971 and 1972. The Reid Gardner station has operated 250 Mw of the system since April 1974, and 125 Mw of the system since July 1976. A letter of intent has been signed for another 125 Mw of new generating capacity at the same station. The system has operated well without any major operating problems. The spent liquor from the process is sent to an unlined sludge settling pond where the brine is evaporated.

In Japan there are 335 sodium scrubbing plants with an average capacity of 20 Mw equivalent and about 500 smaller plants with an average capacity of about 7 Mw. These plants mainly produce sodium sulfite and some sulfate. The product sulfite, in the form of either a concentrated solution or crystal, is sold to paper mills.

The spray dryer (Koyo) process is presently under development by Koyo Iron Works in Japan. It is reported that the process is undergoing a large scale test on an oil-fired boiler at a pulp mill. The use of a spray dryer with a Na_2CO_3 solution to remove SO_2 is also employed in the Atomics International Aqueous Carbonate Process. The spray dryer in this process has been tested at pilot plants treating up to 4000 scfm of flue gas. The use of a spray dryer for SO_2 scrubbing is still not considered commercial technology.

Development work in the U.S. on the dry scrubbing process dates back to the mid-1960's. The dry system has been tested using various modes of contact between the SO_2 and the sodium alkali absorbent. The first tests with injecting nahcolite upstream of a fabric filter for SO_2/SO_3 removal were conducted at a 320 Mw oil-fired unit at the Southern California Edison Alamitos station. The results of the tests were reported to be encouraging. Other testing using this method of SO_2 removal has been done on the pilot scale. The major problem with the process is the inability to achieve more than 60 to 70 percent SO_2 removal.

In 1973 and 1974, the Superior Oil Company built and operated a pilot plant and bench scale facility to test SO_2 removal with a moving bed reactor containing nahcolite. The reactor achieved good SO_2 removal but needs further design and test work to minimize the pressure drop and to determine the maximum allowable inlet particulate loading to the reactor.

Furnace injection of nahcolite has also been tried by Superior with a pilot plant oil-fired burner. SO_2 removal and reagent utilization were high. Agglomeration and fallout of reagent downstream of the burner were observed. There is also the potential of corrosion, erosion, and slagging for direct furnace injection.

Use of Commercialized Technology - The wet scrubbing system is considered commercialized technology. The moving bed, fabric filter, and spray dryer have been industrially demonstrated in different applications but are not considered commercialized technology for SO_2 control. Disposal of Na_2SO_3/Na_2SO_4 sludge in an environmentally acceptable manner is also not considered commercialized technology.

Process Controllability - Both the wet and dry processes are simple chemically and mechanically. The only sodium throwaway process which has sensitive control requirements is the spray dryer. The scrubbing solution for the spray dryer must be carefully controlled as too much will result in condensation in downstream equipment and not enough will prevent attaining the required SO_2 removal efficiency.

ECONOMIC AND TECHNOLOGICAL FACTORS

Comparative process economics were not prepared for these processes as sufficient data were not available. Since these processes involve only SO_2 absorption and solids disposal their actual process costs may be approximated by examining portions of other processes. These processes should be characterized by relatively low capital and relatively high raw material costs.

Capital costs for the wet systems can be compared to costs estimated for the Wellman-Lord and Atomics International Systems. Direct capital investment costs for the wet scrubbing system (without provisions for any specific waste treatment facilities) should be on the same order as those of the Wellman-Lord system without regeneration facilities, or about $15 million. If costs for probable indirect investments and capital charges are included, the total capital investment would become about $30 million. A similar comparison of the expected spray dryer system costs to the Atomics International process results in total capital investment costs of about $32 million. Neither of these costs include charges for solids disposal which will probably raise the process costs by about $15 million, placing them on the same level as costs for a limestone system. Capital costs for the dry fabric filter system were reported by TRW to be on the order of $23 million (including indirects) and capital costs for the moving bed system could not be obtained.

Operating costs will be dictated by the price of the sodium alkali. Due to the high sodium requirements of the dry processes, they may only be economically feasible where a cheap source of sodium exists. Operating costs of the wet processes will be less than those for the dry processes even though they require reheat and have a liquid pumping requirement. However, operating costs may not be less than those of competing non-regenerable systems unless a use for the sodium sulfite/sulfate by-product can be found. Site specific economic evaluations appear warranted.

APPLICABILITY

Suitability for Utility Application - Both the wet and dry processes should be well suited for retrofits. Wet scrubbers, spray dryers, fabric filters, and moving beds all have good turndown capability. Decoupling of process steps should be possible with each process variation. The processing techniques for each process variation should be acceptable to the utility industry since all of the scrubbing concepts have been applied to processes in other industries.

Sodium sulfate is primarily used in the pulp and paper and glass industries. Since this market is small, the Na_2SO_3/Na_2SO_4 sludge utilization is a serious handicap to the process. The Na_2SO_3/Na_2SO_4 salts are soluble and will pose a very difficult disposal problem.

Suitability for Industrial Application - The retrofitability, decoupling ability, and by-product utilization considerations are the same for industrial applications as for utility applications. The processes can all be easily modularized. The sodium throwaway processes should be very well suited to small boiler applications because of the small amount of equipment needed for the process and the resulting low capital cost.

Flexibility to Provide Alternate Products - The process at present does not have the capability to produce either sulfur or sulfuric acid since the Na_2SO_3/Na_2SO_4 is a throwaway product.

Regional/Site Considerations - A major limitation to the process is that it be located near a large source of Na_2CO_3, trona, or nahcolite for economic reasons. All of these sodium minerals are located in the western part of the United States. Therefore, shipping these raw materials to a location in the eastern part of the U.S. would be expensive and possibly prohibitive in cost unless the application was for a low sulfur coal where the sodium alkali requirement was low.

PROCESS ALTERNATIVES

Spray Dryer With Downstream Removal by a Fabric Filter - This alternative combines the advantages of both the wet and dry processes. The spray dryer would be used to insure adequate SO_2 removal due to the larger contact area. The fabric filter is used for downstream collection instead of multicyclones followed by an ESP because of its very high collection efficiency and low energy requirement.

SUMMARY

The sodium carbonate throwaway process is well developed as a wet process but not as a dry process. Further work is needed to optimize and determine the reliability of the dry process using a moving bed and a fabric filter with upstream sodium alkali injection. All of the processes have low energy requirements and are relatively simple. All of the processes except the fabric filter are capable of excellent SO_2 removal. The fabric filter can only achieve 60 to 70 percent removal of SO_2. Difficulty in disposing of the Na_2SO_3/Na_2SO_4 solid waste product in an environmentally acceptable manner is a serious disadvantage to the process. Also, the process may be limited to western locations because the majority of sodium alkali is mined and produced in the western part of the U.S.

SODIUM/LIME DOUBLE ALKALI PROCESS

The sodium double alkali process utilizes a soluble sodium based alkali (NaOH and Na_2SO_3) to absorb sulfur oxides from flue gas in a scrubber. The sulfur-oxide rich effluent liquor is then reacted with a calcium-based alkali to precipitate calcium sulfite, calcium sulfate, and mixed crystals for disposal and to regenerate the sodium based alkali for recycle to the scrubber. The processes developed in the U.S. generally use lime for regeneration, but other processes, developed in Japan, use limestone. These Japanese processes are discussed later in this paper, in the section on Process Alternatives.

The principal reactions are described by the following equations:

Absorption

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \qquad (1)$$

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \qquad (2)$$

Regeneration

$$Ca(OH)_2 + 2NaHSO_3 \rightarrow Na_2SO_3 + CaSO_3 \cdot \tfrac{1}{2}H_2O\downarrow + 3/2\ H_2O \qquad (3)$$

$$Ca(OH)_2 + Na_2SO_3 + \tfrac{1}{2}H_2O \rightarrow 2NaOH + CaSO_3 \cdot \tfrac{1}{2}H_2O\downarrow \qquad (4)$$

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightleftharpoons 2NaOH + CaSO_4 \cdot 2H_2O \qquad (5)$$

$$CaCO_3 + 2NaHSO_3 + \tfrac{1}{2}H_2O \rightarrow Na_2SO_3 + CaSO_3 \cdot \tfrac{1}{2}H_2O\downarrow + CO_2 + H_2O \qquad (6)$$

An important side reaction that also occurs is oxidation:

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \qquad (7)$$

For a concentrated double alkali process, the concentration of active sodium* in the scrubbing liquor is kept above 0.15 molar. Because of the high alkali concentration L/G's are low, typically 5-10 gal/1000 acf of saturated gas. Sulfite oxidation rates as high as 20% of the SO_2 absorbed can be tolerated in the concentrated mode of operation without requiring a separate sulfate removal step. Oxidation rates in this range can be achieved with boilers burning relatively high sulfur coal (2.5% sulfur or greater) with low excess air (O_2 content in flue gas about 4-7%). Dilute systems are generally used for applications where oxidation rates are high. Calcium ions in the regenerated liquor can generally be held to a concentration of less than 100 ppm in a concentrated system. In a dilute system additional softening may be required to prevent $CaSO_4$ scaling in the scrubber. A simplified flow diagram of the double alkali process is shown in Figure 1.

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*Sodium associated with anions involved in SO_2 absorption reactions, including sulfite, bisulfite, hydroxide, and carbonate/bicarbonate.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - SO_2 removal efficiencies greater than 95% have been demonstrated with double alkali processes. The degree of removal can be varied by changing the scrubber operating conditions.

Multipollutant Control - Particulates can be removed simultaneously with SO_2. Envirotech, FMC Corporation, and CEA/ADL have reported simultaneous particulate removal. The particulates reportedly caused no major upsets in process chemistry. A particulate collection device would probably be required before the SO_2 scrubber. The process does not appear to have potential for NO_x removal.

Secondary Pollution Problems; Air - No secondary air pollution problems are anticipated.

Secondary Pollution Problems; Water - The waste solids generated by the process have a high moisture content (near 50%) and contain soluble salts purged from the system. These salts could be leached from the wastes and contaminate surface or ground water in the vicinity of waste disposal sites. There are no direct liquid effluents from the process.

Secondary Pollution Problems; Solid - A large volume of solid wastes is produced. These wastes consist mainly of calcium sulfite, with smaller amounts of calcium sulfate, mixed crystals, and sodium salts, and have a high moisture content. The wastes would probably have to be ponded, with care taken to prevent water pollution as noted earlier. Sludge fixation could possibly be used to reduce the permeability and leachability of the sludge.

Energy Intensiveness - Raw material and utility requirements for the double alkali process are given in Table 1. The calculations are based on the following assumptions:

- Lime utilization - 1.0 mole/mole SO_2 removed.
- Na_2CO_3 makeup - 0.058 mole/mole SO_2 removed. Lower makeup rates (down to about 0.03 mole/mole SO_2 removed) may be possible with efficient cake washing and by reducing fugitive losses to a minimum.

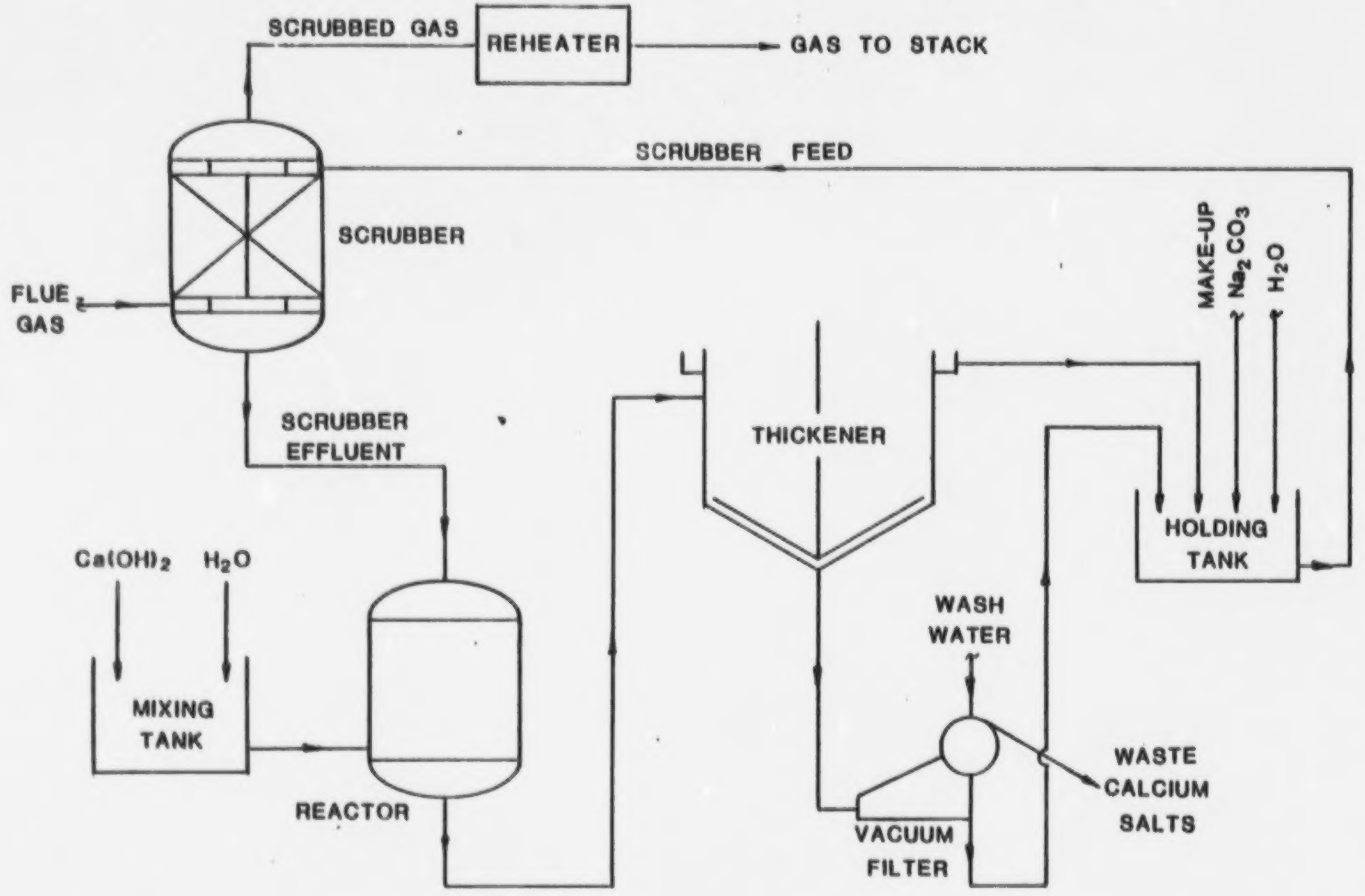
SCRUBBED GAS
REHEATER
GAS TO STACK
SCRUBBER FEED
SCRUBBER
FLUE GAS
MAKE-UP
Na_2CO_3
H_2O
SCRUBBER EFFLUENT
THICKENER
HOLDING TANK
$Ca(OH)_2$
H_2O
WASH WATER
MIXING TANK
WASTE CALCIUM SALTS
REACTOR
VACUUM FILTER

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR SODIUM DOUBLE ALKALI PROCESS

TABLE 1. RAW MATERIAL AND UTILITY REQUIREMENTS FOR SODIUM DOUBLE ALKALI PROCESS

Basis: 500 Mw System, 90% SO_2 Removal, 3.5% Sulfur Coal (Dry)

Raw Materials		
Lime	(tons/hr)	10.7
Soda Ash	(tons/hr)	1.10
Utilities		
Process Water	(10^3gal/hr)	38.0
Electricity	(kw)	
Gas Handling		5207
SO_2 Absorption		1457
Particulate Scrubbing		1086
Miscellaneous[1]		743
Steam[2]	(10^6Btu/hr)	51.1
Solid Waste	(tons/hr)	50

[1] Includes solids separation and disposal, raw material handling and feed preparation.

[2] For flue gas reheat.

Energy is required mainly for fans to overcome gas-side pressure drop in the scrubber and reheater, pumps to circulate scrubbing liquor, and steam to reheat the flue gas. The fan and reheat requirements are similar to those for lime or limestone processes, but the liquid pumping requirements are lower because of the lower L/G made possible by the more concentrated scrubbing solution. Overall, energy requirements for the sodium double alkali process are relatively low compared to other FGD processes.

The water system is operated closed loop because of the presence of soluble sodium salts. Thus, water is consumed principally by evaporation and sludge disposal. Reduction of the water content of the settled sludge could lower overall water consumption significantly.

DEVELOPMENT STATUS

Overall Status - Several vendors in the U.S. have developed sodium double alkali processes. These include Arthur D. Little and Combustion Equipment Associates (CEA/ADL), FMC Corporation, General Motors, Zurn Industries, and Envirotech. A 10 Mw equivalent unit treating gas from reduction kilns was installed by FMC Corporation in December 1971, a 3 Mw demonstration unit on coal and oil-fired industrial boiler was put into operation in January, 1975, and a 45-55 Mw (equivalent) unit on a coal-fired industrial boiler system was started up in October, 1975. General Motors has operated a 32 Mw dilute demonstration system on four coal-fired industrial boilers since March, 1974. Zurn Industries started up a 20-30 Mw equivalent dilute unit on coal-fired industrial boilers in October, 1974. Arthur D. Little and Combustion Equipment Associates, after preliminary pilot work that dealt mainly with characterization of the regeneration reaction, operated a 20 Mw prototype unit on a coal-fired utility boiler from February, 1975, to July, 1976. This work formed the basis for a 277 Mw retrofit unit at Louisville Gas and Electric Cane Run No. 6 that is scheduled for start-up in 1979. This unit will be a full scale utility demonstration for the EPA Double Alkali Research, Development, and Demonstration Program. Two other new installations, a 250 Mw unit designed by FMC and a 575 Mw unit designed by Buell/Envirotech, are scheduled for start-up in 1978 and 1979. The operational units have been integrated.

Double alkali technology is more advanced in Japan, where the sodium/limestone processes developed by Showa Denko and Kureha-Kawasaki has been applied to about 2450 Mw capacity on oil-fired utility and industrial boilers and sulfuric acid plants.

Use of Commercialized Technology - In general, the double alkali process uses technology common to other FGD processes, and the development of double alkali technology benefits from advancements in technology for other soluble sodium scrubbing systems and for lime/limestone systems. ADL has reported, however, that a special regeneration reactor system designed by CEA/ADL gives better settling solids over a wider range of conditions than a simple continuous stirred tank reactor.

Process Controllability - The double alkali process must be controlled to prevent possible problems such as scale formation, sulfate build-up, and poor sludge quality. Gypsum scaling is generally not a problem in concentrated systems since the calcium ion concentration is kept low (less than 100 ppm) by the high sulfite concentration. In dilute systems Na_2CO_3 or CO_2 can be added to the liquor to reduce the calcium ion concentration before it is recycled to the scrubber. Calcium carbonate scaling can occur from the reaction of CO_2 absorbed from the flue gas with dissolved calcium ions. This carbonate scaling can be eliminated by pH control in the scrubber. At scrubber liquor pH below 9 the carbonate/bicarbonate equilibrium tends to limit the concentration of free carbonate ion and thus prevent precipitation of calcium carbonate.

Another problem in double alkali processes results from the oxidation of sulfite to sulfate. Failure to remove the sulfate thus formed can result in eventual precipitation of sodium sulfate in the system or in deterioration of the SO_2 removal capability. Theoretically, sulfates can be removed by precipitation as $CaSO_4 \cdot 2H_2O$, according to Equation (5). In practice, this reaction does not occur to a significant extent in the presence of high concentrations of sulfite ions because the solubility product of calcium sulfite is much lower than that of calcium sulfate. Under certain conditions, however, sulfate is co-precipitated with calcium sulfite in a solid solution. Enough sulfate can reportedly be removed by coprecipitation to allow successful operation with system oxidation rates as high as 20% of the SO_2 absorbed. Other methods that have been developed for sulfate removal are discussed in the Process Alternatives section of this paper.

Poor sludge quality can also be a problem in double alkali systems. Under certain conditions, the waste product solids tend not to settle from the scrubber liquor. This phenomenon is not completely understood, but it is thought to be a function of reactor kinetics. High concentrations of sulfate and magnesium in the liquor also appear to inhibit sludge settling.

ECONOMIC AND TECHNOLOGICAL FACTORS

Estimated capital and operating costs for the sodium double alkali process are given in Tables 2 and 3, respectively. Capital costs were estimated as $50,931,000 and unit revenue requirements as 4.64 mills/Kwh on a utility financing basis. Double alkali costs are in the same range as costs for the limestone scrubbing process, but appear to be somewhat higher for the base case of 90% SO_2 removal. At higher levels of SO_2 removal, however, the double alkali process may be more economical than the limestone process since the concentrated scrubbing liquor used in the double alkali process can achieve better SO_2 removal more easily. Operating costs for the double alkali process are higher than those for the limestone process, chiefly because of the high cost of lime. The cost for lime represents almost 20% of the annual revenue requirements for double alkali; thus, the use of limestone rather than lime for regeneration could potentially reduce operating costs significantly. The use of limestone would, however, increase process complexity and necessitate the use of additional equipment for feed preparation and a larger, more complex reactor system. Capital costs would thus be increased, and could offset the decrease in raw material cost. The Japanese processes that use limestone for regeneration, for example, are complex and expensive. Further research is needed to quantify the overall effect of regeneration with limestone on costs.

Table 2

Sodium/Lime Double Alkali

Total Capital Investment Analysis[a]

	Investment, $
Direct Investment	
Raw materials handling (lime and soda ash receiving, conveyors, storage bins, and pneumatic feed)	945,000
Feed preparation (feeders, conveyors, slakers, tanks, agitators, and pumps)	328,000
Particulate removal (4 venturi scrubbers, tanks, agitators, pumps, and common feed plenum)	3,583,000
Gas handling (4 fans including inlet gas ducts and dampers between fan and plenum, exhaust gas ducts to reheat and ducts to stack)	4,722,000
Sulfur dioxide absorption (4 tray scrubbers including presaturator and mist eliminator, tanks, agitators, and pumps)	3,957,000
Stack gas reheat (4 indirect steam reheaters)	1,071,000
Reaction (tanks and agitators)	371,000
Solids separation (thickener, vacuumfilters, tanks, agitators, and pumps)	2,960,000
Solids disposal (tank, agitator, pumps)	1,825,000
Subtotal	19,762,000
Services, utilities, miscellaneous	1,186,000
Total process areas excluding pond construction	20,948,000
Pond construction	5,803,000
Total direct investment	26,751,000
Indirect Investment	
Engineering design and supervision	1,560,000
Architect and engineering contractor	353,000
Construction expense	3,682,000
Contractor's fees	1,167,000
Total indirect investment	6,762,000
Contingency	6,703,000
Total fixed investment	40,216,000
Other Capital Charges	
Allowance for startup and modifications	3,441,000
Interest during construction	4,826,000
Total depreciable investment	48,483,000
Land	1,025,000
Working capital	1,423,000
Total capital investment	50,931,000

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[a] Basis:
New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).
Coal properties: 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Investment requirements for disposal of fly ash excluded.
90% SO_2 removal; wet venturi particulate removal.

Table 3

Sodium/Lime Double Alkali

Total Annual Revenue Requirements Analysis[a]

Direct Cost	Annual quantity	Unit cost, $	Total annual amount, $
Raw materials			
Lime	75,180 tons	41.00/ton	3,082,400
Soda ash	7,725 tons	90.00/ton	695,300
Total raw materials cost			3,777,700
Conversion			
Operating labor and supervision	29,300 man-hr	12.50/man-hr	366,300
Utilities			
Steam	358,000 MM Btu	2.00/MM Btu	716,000
Process water	266,200 M gal	.12/M gal	31,900
Electricity	59,439,000 kwh	0.029/kwh	1,723,700
Maintenance, 5% of direct investment			1,337,600
Analyses	4,400 man-hr	17.00/man-hr	74,800
Total conversion costs			4,250,300
Total direct costs			8,028,000
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6% of total depreciable investment			2,909,000
Average cost of capital and taxes at 8.6% of total capital investment			4,380,100
Overhead			
Plant, 50% of conversion costs less utilities			889,400
Administrative, 10% of operating labor			36,600
Total indirect costs			8,215,100
Total annual revenue requirements			16,243,100

	Dollars/ton coal burned	Mills/kwh	Cents/million Btu heat input
Equivalent unit revenue requirement	10.83	4.64	51.6

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a. Basis:

New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up).
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned: 1,500,100 tons/yr, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Total capital investment, $50,931,000; total depreciable investment, $48,483,000; total direct investment, $26,751,000.
Investment and revenue requirements for disposal of fly ash excluded.
90% SO_2 removal; wet venturi particulate removal.

APPLICABILITY

Suitability for Utility Application - Double alkali systems may be somewhat easier to retrofit than lime/limestone systems since, because of the lower liquid-to-gas ratio, smaller equipment is used to contact the flue gas. However, a large amount of land is required to dispose of the calcium sulfite waste sludge. Turndown capability of the scrubber should be very good. The regeneration system and solids handling equipment can be decoupled from the absorption system by intermediate storage.

Suitability for Industrial Application - Considerations affecting industrial retrofitability, by-product utilization, and decoupling ability are similar to those for utility application. The process should have the capability for modularization. It has been applied successfully to small industrial boilers.

Flexibility to Provide Alternate Products - The process produces a calcium sulfite sludge, but can be modified to produce gypsum.

Regional/Site Consideration - The only regional consideration that may limit applicability is the availability of land for sludge disposal.

PROCESS ALTERNATIVES

Sulfate Removal - Various sulfate removal techniques have been investigated. In dilute systems, with active alkali concentrations less than 0.15 molar, sulfates can be removed by precipitating calcium sulfate with the addition of lime, according to reaction (5). In a dilute system, however, because of the lower concentration of alkali in the scrubbing liquor, large volumes of scrubbing liquor must be circulated through the absorber to achieve good SO_2 removal. These large volumes must also be circulated through the regeneration and solid/liquid separation equipment. Capital and operating costs for SO_2 removal would thus be higher for dilute systems. However, costs for waste disposal could be lower since dilute systems produce sludge with a high gypsum concentration. In the Buell-Envirotech process, spent scrubbing liquor is oxidized to further increase the concentration of sulfate before it is reacted with lime. The waste solids produced would thus have an even higher concentration of gypsum. Dilute systems are more prone to scaling than concentrated systems because the scrubbing liquor in dilute systems has a higher concentration of dissolved calcium ions. To reduce the scaling potential, the scrubbing liquor is softened by addition of Na_2CO_3 or CO_2 to remove calcium ions as $CaCO_3$ before the liquor is recycled to the absorber.

Another sulfate removal method uses sulfuric acid to dissolve calcium sulfite, increasing the concentration of calcium ions in solution enough to exceed the solubility product of calcium sulfate. The method does require more H_2SO_4 than the stoichiometric amount indicated by reaction (8) and also increases calcium consumption.

$$Na_2SO_4 + 2CaSO_3 \cdot \tfrac{1}{2}H_2O + H_2SO_4 + 3H_2O \rightarrow 2NaHSO_3 + 2CaSO_4 \cdot 2H_2O \qquad (8)$$

This is the sulfate removal method used in the Japanese double alkali processes. Sulfates could also be removed as sulfuric acid in an electrolytic cell by the Ionics process:

$$Na_2SO_4 + 3H_2O \xrightarrow{\text{Electrolytic Cell}} 2NaOH + H_2SO_4 + H_2 + \tfrac{1}{2}O_2 \qquad (9)$$

This method would require a significant amount of electrical energy. The sulfuric acid and electrolytic cell techniques of sulfate removal help to decrease sodium losses from the system, but require additional raw materials or energy that add to system operating costs. Another approach to sulfate removal may be to limit oxidation sufficiently so that sulfates can be controlled by a small purge of Na_2SO_4 with the waste product, but disposal of the Na_2SO_4 would be difficult and cost of anti-oxidants could be high.

Forced Oxidation - The quality of the solid wastes produced can be improved by forced oxidation of the calcium sulfite to calcium sulfate (gypsum). Sludges containing a high ratio of calcium sulfate to calcium sulfite are less thixotropic than sludges having a higher proportion of calcium sulfite, and can also be settled, filtered, and dewatered more easily. In addition, calcium sulfate or gypsum has a higher compressive or bearing strength and is suitable for landfill disposal. In Japan, forced oxidation has been used to produce gypsum solid wastes suitable for wallboard or cement production. A liquor purge stream may be necessary to prevent the build-up of soluble species in systems using forced oxidation since little water is discharged with the solid wastes. This purge stream, however, would be no larger than the amount of water discarded with conventional sludges.

Regeneration with Limestone - The double alkali processes developed in the U.S. generally use lime for regeneration, but the use of limestone has been investigated in laboratory tests by A. D. Little. The full scale processes developed in Japan utilize limestone for regeneration. They also use forced oxidation of calcium sulfite to produce gypsum. Sulfuric acid addition is used for sulfate removal. In these processes, flue gas is scrubbed with a solution of Na_2SO_3. A bleed stream from the scrubber is neutralized with limestone to regenerate the Na_2SO_3 and precipitate calcium sulfite. The calcium sulfite is reslurried, acidified with sulfuric acid to reduce the pH and dissolve calcium sulfite, and oxidized with air to produce gypsum. The gypsum is dewatered to 5-10% moisture in a centrifuge. A small slip stream of scrubber effluent is reacted with calcium sulfite and sulfuric acid to remove sulfate. This combination of processing steps makes the processes relatively complex and expensive. High levels of oxidation in the scrubber can be tolerated, but are uneconomical because of the expense of sulfuric acid addition and the additional limestone required for neutralization.

The gypsum product is sold for cement or wallboard production in Japan, but in the U.S. it probably could not be marketed. Because of the low moisture content, it would be suitable for landfill disposal. Since little water is discharged with the waste product, however, a purge stream will be necessary to limit the concentration of chloride and magnesium in the system.

Magnesium enters as an impurity with the limestone, and tends to delay the reaction of limestone with sodium bisulfite in the regeneration step. Limestone is a cheaper raw material than lime, but is less reactive so that larger reactors and a more complex reactor system are required. In addition, limestone occurs in a variety of forms varying in reactivity. Process control may thus be more difficult with limestone than with lime. More solid wastes would also be produced with limestone. Nevertheless, the use of limestone may be an attractive alternative if it can be accommodated with a reasonable degree of increase in process complexity, control requirements, and capital costs.

Alternate Absorbents - Scrubbing solutions that do not have a sodium base have been used in double alkali-type systems. Ammonia based scrubbing solutions have the advantage that ammonium sulfate is readily decomposed by lime, but the formation of a visible plume by the highly volatile ammonium compounds presents a major problem. Kurabo Industries, however, has developed a process that eliminates plume formation by scrubbing with a slightly acidic ammonium sulfate solution. Monsanto's Calsox Process uses an aqueous organic base in the scrubbing solution. The Dowa process uses basic aluminate sulfate, $A\ell_2(SO_4)_3 \cdot A\ell_2O_3$, to absorb SO_2, forming $A\ell_2(SO_4)_3 \cdot A\ell_2(SO_3)_3$. The liquor is oxidized to form $A\ell_2(SO_4)_3$ which is then treated with limestone to precipitate gypsum and regenerate the basic aluminum sulfate solution. The Kureha Chemical Process uses a sodium acetate solution as the absorbent to achieve SO_2 removal efficiencies of more than 99%. The Kurabo and Dowa Processes are discussed in separate technical summary papers.

SUMMARY

The sodium double alkali process uses a concentrated, clear solution of a soluble alkali to scrub SO_2. The concentrated scrubbing liquor achieves good SO_2 removal at a relatively low liquid to gas ratio. The clear scrubbing solution can be treated to eliminate scaling and minimize solids buildup and erosion problems, thus improving reliability of operation. Since the reactions with lime (or limestone) occur in specially designed reactors rather than in the scrubber, lime (or limestone) is utilized more efficiently in double alkali processes than in direct lime/limestone scrubbing processes. As with lime/limestone processes, the disposal of the solid waste product presents a significant environmental and land management problem. Because of the presence of soluble sodium salts in the scrubbing liquor, waste solids from the double alkali process may have a relatively high concentration of these salts and thus present a potential water pollution problem. If the oxidation rate is too high to allow sufficient removal of sulfates by co-precipitation with calcium sulfite, other sulfate removal methods (such as sulfuric acid addition) would be necessary. The Japanese double alkali processes that use limestone for regeneration are more developed than the American sodium/lime processes and produce a better waste product, but they are also more complex and probably more expensive. Major areas for further research appear to be in improving the characteristics of the waste (forced oxidation, for example) and in acquiring more operating experience with the process. Further research should also be done on the use of limestone as a regenerant.

References - AN-147, AN-187, BL-110, CO-163, KA-143, KA-227, LA-081, LA-108, LA-134, LA-238, LE-235, PE-259, RO-190, SA-236.

SORPTION/STEAM STRIPPING PROCESSES

A number of process alternatives exist for a sorption/steam stripping FGD system. These alternatives differ primarily in the sorbent used. Several process options and their respective absorbents are listed below:

- NIIOGAZ Ammonia/Steam Stripping - Ammonia
- ICI Steam Stripping - Base - Aluminum Sulfate/Aluminum Chloride Solution
- Peabody - Sodium Citrate
- Ethylenediamine System - Ethylenediamine
- Spring - Nobel Hoechst - Gloxylic Acid

In addition to these absorption processes, Rohm & Haas has proposed an adsorption process based on the use of a resin absorbent.

A generalized configuration for the sorption/steam stripping process is shown in Figure 1. Flue gas is prescrubbed with water to remove HCl, SO_3, residual fly ash, and possibly NO_2. SO_2 is removed by absorption in an aqueous solution in a countercurrent absorber with 10-20 feet of packing or 3-6 trays. The gas is reheated to 175°F by any acceptable method. The feed solution to the scrubber usually corresponds to an L/G less than 10 gal/MCF, and frequently recirculation loops are required to maintain adequate liquid loading on the packing or trays. The scrubber feed and SO_2-rich solutions are cross-exchanged for optimum heat recovery. Intermediate storage of the rich and lean solutions permits decoupling of scrubber operation from solution regeneration. The SO_2-rich solution is stripped with live steam in a countercurrent packed or tray column. Water is condensed from the stripper overhead, stripped in a small column with a small amount of steam and vaporized to produce live steam for the main stripper. Normally the SO_2 product will be a gas containing about 95% SO_2 and 5% H_2O. If stripping is performed at a pressure greater than 4 atmospheres, liquid SO_2 (containing some H_2O) can be directly produced. Intermediate storage of liquid SO_2 permits decoupling of the stripper from further processing.

The SO_2 product is suitable for conversion to sulfuric acid or elemental sulfur. Sulfuric acid production would use mostly conventional technology with some modifications required to use the more concentrated SO_2. Sulfur production could use developing processes such as Allied (CH_4 reduction) or Resox (anthracite reduction).

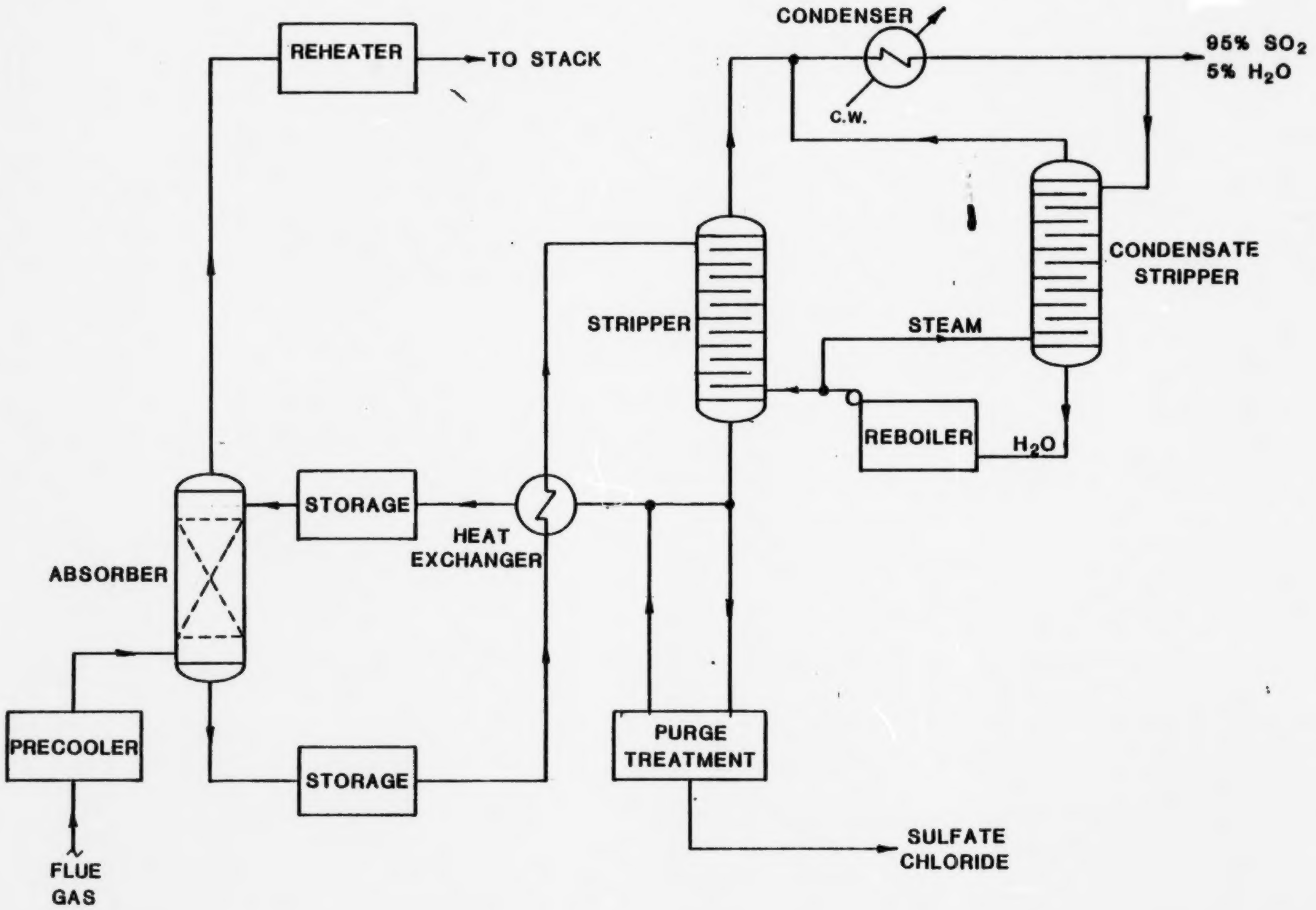
REHEATER
TO STACK
CONDENSER
C.W.
95% SO_2
5% H_2O
CONDENSATE STRIPPER
STRIPPER
STEAM
REBOILER
H_2O
ABSORBER
STORAGE
HEAT EXCHANGER
STORAGE
PRECOOLER
FLUE GAS
PURGE TREATMENT
SULFATE CHLORIDE

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR ABSORPTION/STEAM STRIPPING PROCESS

Any sulfate formed in the scrubber or stripper and any residual HCl or SO_3 removed in the scrubber will accumulate in the system and must be removed from the aqueous-absorbent and sent to disposal. At normal conditions with a sulfite/bisulfite solution typical of the Wellman-Lord process, 2-10% of the absorbed SO_2 is oxidized to sulfate in the scrubber. This level of oxidation can probably be expected from these processes, as well. Some developers of steam stripping processes claim lower levels of oxidation, but these are probably not valid in most cases. Past experience has also generally shown that the stripper must be operated at a temperature less than 212°F to avoid disproportionation of bisulfite to sulfate and thiosulfate. Sulfate is most frequently removed from a slipstream by crystallization of salts such as Na_2SO_4 or $CaSO_4$. No developers have specific plans for removing chlorides, but a solution purge will probably be utilized. Accumulation of chlorides would probably make 316 stainless steel an unacceptable material of construction.

Flue Gas Cooling - Commonly the flue gas is cooled to 120-130°F by adiabatic saturation with water. However, vapor-liquid equilibrium characteristics of some of the absorbent alternatives {$Al_2(SO_4)_3$, glyoxylic acid, and $(NH_4)_2SO_3$} require nonadiabatic gas cooling to 95-105°F to assure reasonable steam requirements and/or adequate absorber performance. This is most easily accomplished by using a countercurrent (packed) prescrubber with a heat exchanger in which the recirculating solution is cooled by utility cooling water. One scheme involves the use of a very concentrated solution such as $CaCl_2$, $MgCl_2$, or $AlCl_3$ in the prescrubber loop. This concentrated chloride solution can be circulated at a relatively high temperature, thus maximizing the temperature difference available for heat exchange with process cooling water. The concentrated chloride solution is also quite effective at lowering the flue gas saturation temperature. However, because of the low pH (1-3) and high chloride concentration, the heat exchanger must use expensive, corrosion-resistant materials such as Incoloy 825.

With adiabatic gas cooling to 125°F, reheat to about 175°F is required to avoid corrosive condensation in the stack and enhance plume dispersion. With nonadiabatic gas cooling an equivalent amount of reheat from 95°F to 150°F should be adequate to avoid condensation in the stack, though additional reheat could be used to give better plume rise.

Absorbent Alternatives - There are five representative absorbent alternatives which could be used in the general flowsheet with only minor flowsheet modifications. Three of these require gas cooling, {$Al_2SO_4)_3/AlCl_3$, glyoxylic acid, $(NH_3)_2SO_3$}, and two do not (sodium citrate, ethylenediamine sulfate).

$Al(OH)_3$ solutions containing high concentrations of $Al_2(SO_4)_3$ and/or $AlCl_3$ buffer at pH 3-4.5 are suitable for SO_2 absorption as bisulfite at 95-105°F (Applebey, 1937). Sulfate is removed from this solution by neutralization with $CaCO_3$ to produce gypsum. Chloride could be removed by further neutralization to precipitate $Al(OH)_3$ solids and leave $CaCl_2$ solution for purge. However, because aluminum makeup probably as $Al(OH)_3$ is relatively inexpensive, direct purge of $AlCl_3$ solution is economically feasible. Furthermore, because of the ease and low cost of sulfate/chloride removal, it may not be necessary to separate prescrubber solution from the absorber solution.

Glyoxylic acid (O=CH-COOH) absorbs SO_2 as hydroxy-sulfo-acetic acid ($H^+ \ {}^-O_3S$-CHOH-COOH) at pH 1-2 and 35°C (RO-333). Low scrubbing temperature appears necessary for adequate scrubber performance, probably because SO_2 absorption at the low pH is controlled by liquid-phase mass-transfer resistance. Because little free SO_2 or bisulfite is contained in the scrubbing solution, sulfate formation by oxidation in the absorber and disproportionation in the absorber should be minimized. Claims of negligible oxidation in this system are probably valid. However, there is no clear evidence on the stability of glyoxylic acid in the presence of O_2 and NO_x, particularly with respect to oxidation to oxalic acid (HOOC-COOH). Sulfate could easily be removed as gypsum by neutralization with limestone.

Ammonium sulfite $(NH_4)\ SO_3$ effectively absorbs SO_2 as bisulfite at temperatures up to 150°F. ($SO_3^= + SO_2 + H_2O \rightleftarrows 2HSO_3^-$). However, low absorption temperature (95°F) is necessary to give greater conversion of sulfite to bisulfite. The more volatile bisulfite is more readily stripped from the liquor, hence steam requirements for solution regeneration are lessened. Furthermore, lower absorber temperature should significantly reduce problems with ammonia volatility, fume formation in the scrubber, and oxidation of absorbed SO_2 to sulfate. Sulfate can be removed from this system by lime neutralization to give gypsum or dry crystallization of marketable ammonium sulfate. Solution purge would probably be used for chloride removal.

Sodium citrate solution at pH 4.5-6 is effective for SO_2 absorption at adiabatic saturation temperature. Peabody claims quite reasonable steam requirements with absorption at 125°F and stripping at 265°F and this evaluation assumes no gas cooling would be necessary. However, there is some uncertainty in Peabody's claims. Sulfate is removed by refrigerated crystallization of Glauber's salt ($NA_2SO_4 \cdot 10H_2O$). No specific suggestions have been made for chloride removal.

Ethylenediamine sulfate at pH 5-6 and 125°F is an effective absorbent for SO_2 and should give reasonable steam requirements because it is a weak base which becomes more acid at higher temperature. Sulfate would be removed by neutralization with lime to give gypsum. Chlorides could be removed as $CaCl_2$ solution by lime adjustment to pH 11 followed by evaporation of free ethylenediamine.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - Most of the steam stripping alternatives should be capable of excellent SO_2 removal (95 +%) without any significant energy or equipment penalties. However, the higher removal efficiencies are probably more difficult to achieve in the system using ammonium sulfite/bisulfite because complete solution stripping is not possible.

Multipollutant Removal - None of the process alternatives have any unique features suitable for NO_x removal. Particulates and chlorides are generally removed before the absorber.

Secondary Pollution Problems; Air - Fume formation is a problem with NH_3 scrubbing. Because of the lower gas temperature (95°F), fume formation will be much less of a problem than it is with NH_3 absorbers operating at 120-140°F.

Volatility and possible losses of glyoxylic acid and ethylenediamine in the scrubber are possible problems. However, both of these organics are very hydrophilic and therefore less volatile when in water solution. Furthermore, each molecule of ethylenediamine would be protonated at scrubber conditions, resulting in even less volatility.

Secondary Pollution Problems; Water - Toxicity of the absorbents could cause some problems. Specifically, glyoxylic acid or ethylenediamine have unknown side-effects, but neither of these is known to be especially toxic. Furthermore, economic system operation requires that losses be minimized.

Secondary Pollution Problems; Solid - All of these systems require disposal of a sulfate waste product, usually gypsum. However, scrubbing with glyoxylic acid should give a lower rate of sulfate formation than the other systems, because the rich scrubbing solution contains little sulfite or bisulfite.

Energy Intensiveness - Raw material and energy balance calculations are presented in Table 1. Absorbent makeup requirements are generally unknown, so they have been estimated as being equivalent to 1 mole absorbent/100 moles SO_2. In practice, systems with more expensive absorbents will require greater care to avoid losses. Lime requirements and gypsum production match the need for sulfate removal at the rate of 5 moles/100 moles SO_2 for all absorbents but glyoxylic, which assumes 1 mole sulfate/100 moles SO_2. Electricity requirements for fans and pumps reflect the need for nonadiabatic gas cooling $Al(OH)_3$, glyoxylic acid, NH_3 and for greater mass transfer capability (glyoxylic acid).

TABLE 1. ESTIMATED RAW MATERIAL AND ENERGY REQUIREMENTS FOR STEAM STRIPPING PROCESSES

Basis: 500 Mw, 3.5% S Coal, 90% SO_2 Removal, 3.5% Sulfur Coal (dry)

	base-$Al_2(SO_4)_3$	Glyoxylic Acid	NH_3	Sodium Citrate	Ethylene-diamine
Raw Materials					
Absorbent Cost					
($/lb mole)	6	100	1.50	69	44
(mills/kwh)[1]	0.04	0.71	0.01	0.49	0.31
CaO (lbs/hr)	1000	200	1000	1000	1000
Electricity (Mw)	12.5	15	12.5	10	10
Steam (MLBS/hr)					
Reheat (500 psig)	90	90	90	90	90
Stripping (25 psig)	60	60	160	250	160
Process Water (Mgal/hr)	0	0	0	25	25
Cooling Water (Mgal/hr) (20% rise)	1875	1875	2500	1560	1000
Solid Waste (gypsum) (lbs/hr)	2750	550	2750	2750	2750

[1] Absorbent loss estimated as 0.01 moles/mole SO_2 removed.

Steam requirements for reheat are assumed to be identical for all of the processes. Gas from systems using nonadiabatic gas cooling would not be reheated to as high a temperature. Because of the lower water content of the colder gas, this procedure is consistent with avoiding condensation in the stack and steam plume formation.

Stripping steam requirements were estimated from data supplied by Spring and Peabody and from fundamental relationships. In comparison, the Wellman-Lord process requires 225,000 lbs steam/hour under comparable conditions. Thus, Table 1 shows that only the sodium citrate system appears not to have the potential for lower steam consumptions compared to Wellman-Lord. Process and cooling water requirements reflect differences in gas cooling and stripping steam requirements.

DEVELOPMENT STATUS

Overall Status - Though many of these processes have only been briefly tested, or are at the conceptual stage, their development to commercial processes could be quite rapid. The general problems of aqueous scrubbing such as reheat, wet/dry interfaces, and fan design should be resolved in applications of throwaway scrubbing. Applications of the Wellman-Lord and Citrate Buffered Processes should resolve prescrubber design as well as reduce uncertainties about oxidation. Furthermore, a single steam stripping development facility could be used to test a number of alternative absorbents. There are three remaining areas requiring general development work:

1) Absorber/stripper sizing.
2) Uncertainties in sulfate formation.
3) Testing of nonadiabatic gas cooling.

In addition, each of the absorbents may have its own unique problems and developments.

- Aluminum Sulfate System - In the late 1930's, I.C.I. developed and commercialized a steam stripping process using aluminum sulfate solution (Applebey, 1937). The process was applied to SO_2 removal from a smelter stack gas. More recently, Dowa has commercialized a throwaway scrubbing process using aluminum sulfate solution on oil-fired boilers in Japan. I.C.I. has specifically identified and resolved problems with precipitation and scaling of several basic aluminum sulfate salts.

  Published data on liquid/vapor equilibrium in this system are quite limited and need to be extended to higher temperature levels (125-200°F) and lower SO_2 gas concentrations (100-2000 ppm). Pilot plant development would be necessary to demonstrate nonadiabatic gas cooling and to reestablish the technology with current equipment. Prototype development would probably be required to establish the rate of sulfate formation.

- Glyoxylic Acid System - This process is being developed by a joint venture of Spring Chemical (Canada) and Nobel-Hoechst (France). A small pilot plant (300 scfm) is being operated on the tail gas of a sulfuric acid plant. There are plans to use the pilot plant on coal-fired flue gas.

  Design of absorption/stripping systems for using glyoxylic acid requires information on liquid-side mass transfer coefficients and rates of chemical reaction, in addition to data on liquid/vapor equilibria. These data may have been developed by Nobel-Hoechst, but have not been publicly released. Pilot plant testing of this process on coal-fired flue gas is necessary to demonstrate nonadiabatic gas cooling, verify low levels of sulfate formation, verify materials of construction, and identify any problems with absorbent stability or volatility.

- Ammonium Sulfite/Bisulfite System - A great deal of work has been done on ammonium sulfite/bisulfite scrubbing and steam stripping. The Russians have operated a 50 Mw unit on a coal-fired boiler. They used an open-loop system for nonadiabatic gas cooling which would not be generally acceptable in the U.S. A wet electrostatic precipitator was used to remove fume from the cleaned gas. Thus, fume formation did contribute to the complexity and cost of the process.

  Pilot plant development would be required to establish the degree of scrubber complexity required to control fume formation at 95°F and to demonstrate a practical means of nonadiabatic gas cooling. Additional data on SO_2 removal and steam requirements are not needed, though more information on sulfate formation would be useful. Prototype or commercial demonstration of sulfate removal by lime addition would also be desirable.

- Sodium Citrate System - The use of sodium citrate in a steam stripping system has followed directly from its use with H_2S regeneration. The Bureau of Mines at Salt Lake City is testing the process in a bench-scale absorber/stripper at atmospheric pressure. Peabody supported a brief test of stripping at elevated pressure to reduce steam requirements and produce liquid SO_2.

Available liquid/vapor equilibrium data are suitable for absorber design but additional data at 200-265°F need to be generated for stripper design. Pilot or prototype scale testing on coal-fired flue gas is necessary to establish the level of sulfate formation. It is unlikely that pressurized stripping will be feasible because of the much faster rate of bisulfite disproportionation to sulfate and thiosulfate at elevated temperatures.

- Ethylenediamine System - This is a conceptual absorbent briefly tested in the 1930's. Liquid/vapor equilibrium data need to be generated. Bench scale development should also identify any solubility problems and characterize any unique problems of bisulfite disproportionation, which may be catalyzed by the amine. Pilot or prototype testing with coal-fired flue gas is necessary to establish the level of sulfate formation and test sulfate removal.

Use of Commercialized Technology - Design of absorbers and strippers for these processes is usually based upon gas/liquid equilibria and gas-phase mass transfer. Thus, when using conventional contactors such as packed and tray columns, reliable design for SO_2 removal and steam requirements needs only the gas/liquid equilibrium data for each system. These data can be generated in the laboratory and immediately used in full-scale design. Reliable data are available for ammonium sulfite/bisulfite, but would need to be generated for the other systems.

Process Controllability - There are few data on the amount of sulfate formation that should be expected in these systems. Uncertainties include the effects of NO_x, the role of O_2 mass transfer, the importance of solution pH and bisulfite concentration, and factors resulting in disproportionation. Reliable data on the questions can only be answered by operating closed-loop, prototype or demonstration units cleaning actual flue gas from coal-fired boilers. Some conclusions can be drawn from operation of the Wellman-Lord and Citrate demonstrations. However, each absorbent and regeneration system will probably give somewhat different results.

The use of nonadiabatic gas cooling with the base-$Al_2(SO_4)_3$, glyoxylic acid, or ammonia absorbents introduces significant problems with materials of construction. Reliable operation of a heat exchange surface in contact with a warm, low pH, concentrated chloride solution may be quite difficult. This system needs to be demonstrated in a pilot plant with actual, coal-fired flue gas.

ECONOMIC AND TECHNOLOGICAL CONSIDERATIONS

Comparative cost estimates were not developed for the absorption/steam stripping processes due to lack of data. Captial costs for these processes should be comparable to those for the Wellman-Lord process in that the absorption/steam stripping processes employ a scrubber and prescrubber, a thermal regeneration system, some type of purge treatment, and an SO_2 processing facility. Steam stripping process costs may be slightly less than Wellman-Lord due to their overall simpler process operations. Exceptions to this are the steam stripping processes requiring flue gas precooling and thus expensive construction materials to reduce corrosion problems.

Operating costs cannot be well defined as it is not now known exactly what the steam requirements and absorbent makeup rates will be for the absorption steam stripping processes. It is expected that the processes requiring flue gas precooling to 95-100°F will have lower steam requirements than the processes cooling flue gas only to its adiabatic saturation temperature. The cost benefits from steam savings for these processes may not, however, completely offset the cost deficits resulting from the requirement for specialized construction materials. More data are needed on these processes so that a detailed economic assessment can be made.

APPLICABILITY

Suitability for Utility Application - Steam stripping systems are usually suitable for decoupling by installing intermediate storage. Turndown capability and suitability for retrofit should be good. The stripping operation can be located on the power plant site, but remote from the boiler, so space requirements at the boiler include only the absorbers and their auxiliary equipment. Utility acceptability should be comparable to other wet regenerative processes.

Suitability for Industrial Application - Considerations affecting industrial applications are much the same as for utility application. Although the absorbers and steam strippers can be readily modularized, the cost of processing SO_2 to sulfur or sulfuric acid is high and thus the steam stripping processes would not be generally applicable to smaller boilers unless a centralized SO_2 processing facility could be used.

Flexibility to Provide Alternate Products - These processes are capable of providing liquid SO_2, sulfur, or sulfuric acid.

Regional/Site Considerations - Steam stripping is most attractive with gases of higher SO_2 concentration at lower temperature, because steam requirements are generally reduced by these conditions. Thus, these processes would be relatively more attractive with very high-sulfur coal or with dry, cool gas such as tail gas from sulfuric acid plants and they are relatively less attractive for low-sulfur coal applications.

PROCESS ALTERNATIVES

Heat Recovery - Steam requirements for most of these systems can be reduced by a variety of methods that generally increase the complexity and capital cost of the process. Double-effect strippers reuse steam heat at lower pressures and would require additional vacuum equipment, but could reduce steam requirements by about 40 percent. Because only low-pressure atmospheric steam is required for stripping, it is attractive to use exhaust steam from pump and fan driven turbines. Also, heat could be recovered from the stripper overhead gas for boiler feedwater preheat, low pressure steam for power turbines, or flue gas reheat. However, the degree of integration required to use the methods probably will make them unattractive.

Reboiled Stripper - Most of the process developers have used evaporation of stripper bottoms solution to produce steam. This method may be attractive for reducing stripper height requirements with high capacity solutions. A reboiled stripper also permits return of condensate to the stripper overhead and eliminates the need for a condensate stripper. However, evaporation of stripped condensate should usually be more attractive because the evaporator can be constructed of mild steel. A stripper bottoms reboiler would require more expensive corrosion-resistant materials of construction. The residence time and disproportionation of the absorbing solution should be minimized by avoiding solution evaporation through use of a condensate stripping system.

Solution evaporation can be quite attractive if solids are crystallized as in the Wellman-Lord process. With the crystallization of basic solids such as Na_2SO_3 (Wellman-Lord), $(NH_4)_2SO_3$, or amine sulfite, the overhead condensate is used to redissolve the solids for scrubbing. With the crystallization of acid solids such as $K_2S_2O_5$ or adipic acid, the condensate should be returned to the top of the stripper.

Absorbent Alternatives - There are a number of alternatives to the five basic absorbents of current interest. These can be classified as strong bases, acid buffers, weak bases, or aldehydes.

The relatively strong bases (Na_2CO_3, ethanolamine, methylamine, or KOH) can be substituted for ammonia in a system based upon sulfite/bisulfite solutions. Steam requirements would probably be somewhat higher and sulfate might be more difficult to remove, but problems with ammonia volatility and fume formation would be avoided.

Acid buffers other than citric acid could be effectively used. The important alternatives include phosphate, adipate, and phthalate. Insufficient information is available on these alternatives to estimate their effects on steam requirements. They could potentially reduce the cost of buffer makeup.

The ethylenediamine and base-$AlCl_3/Al_2(SO_4)_3$ solutions are weak bases considered in this evaluation. Dimethlaniline has been commercially used as a nonaqueous, weak base absorbent by ASARCO in smelter application. However, it and other aromatic amines are too volatile to be of practical interest for power plant applications. Monsanto did bench scale work on a process using ethanolamine glutarate as an absorbent, but development of the process, NOSOX, has been discontinued. There is some potential for identification of other, inexpensive, nonvolatile organic amines with proper buffering characteristics.

Glyoxylic acid is one of several aldehydes that would be relatively nonvolatile in aqueous solution. Nobel-Hoechst also has a patent on glyoxal (O=C-C=). The alternatives are potentially less costly and could have different absorption characteristics.

Adsorption/Steam Stripping - Rohm & Haas is doing conceptual design work on a resin adsorption process for flue gas SO_2 removal. Regeneration would be accomplished by steam stripping the spent resin. The developers claim that, since SO_2 sorption is accomplished by physical complexing with the resin rather than by chemical reaction, steam requirements for regeneration are reduced. However, since the process is only at the conceptual stage, no performance or economic data are available.

SUMMARY

SO_2 removal from stack gas by absorption/stripping has been considered intermittently since work by H. F. Johnstone in the 1930's. Early work commercialized systems using aluminum sulfate solutions and aromatic amines. The Russians have tested a full-scale ammonium sulfite/bisulfite absorbent. Sodium citrate and glyoxylic acid absorbents are currently being actively proposed by Peabody and Spring Chemicals, respectively. Process advantages are its relative simplicity and reported low energy requirements; disadvantages are its current lack of development and process data. RD&D efforts for these processes should probably be centered in the following areas: developing process data on steam and absorbent requirements; developing data on sulfate formation for the various systems; analysis of the effects of nonadiabatic gas cooling; and developing a set of comparable process economics.

References - AP-029, JO-003, JO-111, KI-160, RO-033, ST-409

SULF-X PROCESS

The Sulf-X process simultaneously removes SO_2 and NO_x by scrubbing with ferrous sulfide. Due to the early development status of the process, an overall process design for a large scale plant has not yet been finalized. Consequently, the following represents engineering judgment and developer claims as to actual process configuration and performance.

Flue gas at 250-300°F is subjected to particulate removal in a cold ESP and then contacted with a ferrous sulfide-water slurry in a venturi quench vessel to cool the flue gas to adiabatic saturation temperature. The process developer has indicated that it may be possible to eliminate the ESP and replace it with a venturi. This would increase fly ash loading throughout the system and the cold ESP may be the most viable alternative.

The gas is then contacted with a slurry of FeS in either a venturi, packed tower or tray tower for SO_2 and NO_x removal. The following overall reactions have been reported by the process developer:

$$5FeS + SO_2 + 2H_2O \rightarrow 3FeS_2 + 2Fe(OH)_2 \qquad (1)$$

$$4FeS + 2NO + 2H_2O \rightarrow N_2 + 2\ FeS_2 + 2Fe(OH)_2 \qquad (2)$$

$$8FeS + 2NO_2 \rightarrow N_2 + 4FeO + 4FeS_2 \qquad (3)$$

It should be emphasized that these reactions are overall reactions and do not include a number of intermediate reactions that the process developer reports are proceeding in the system. At pH of about 5.5 the following secondary reactions become important:

$$2FeS + 6SO_2 + 4H_2O \rightarrow 2FeS_2 + 4H_2SO_4 \qquad (4)$$

$$Fe(OH)_2 + H_2SO_4 \rightarrow FeSO_4 + 2H_2O \qquad (5)$$

$$2FeSO_4 + H_2SO_4 + NO \rightarrow Fe_2(SO_4)_3 + H_2O + \tfrac{1}{2}N_2 \qquad (6)$$

It is anticipated that the scrubber pH would be controlled at 5.5 by varying scrubber liquor feed rates. The scrubbed gas is then reheated and routed to the stack. Although the spent sorbent could be disposed of as landfill in some specific situations where large quantities of FeS are readily available, it is anticipated that the spent absorbent will be regenerated in most power plant applications. Consequently, this option is addressed here. The spent absorbent is taken to a thickener so that fly ash is removed, filtered and disposed of. Some FeS would also be lost with this stream.

The thickened slurry is sent to a filtration or centrifugation unit and then to a regeneration kiln. In the regeneration kiln, the iron sulfide is regenerated with carbon (such as coal fines) by the following representative reactions:

$$2Fe(OH)_2 \xrightarrow{\Delta} 2FeO + 2H_2O \qquad (7)$$

$$3FeS_2 + 2FeO + C \rightarrow 5FeS + CO_2 + S^0 \qquad (8)$$

The resulting dry FeS is then reslurried and returned to the absorber section. Off gas from the regeneration kiln is routed to a cyclone for particulate removal and to a condenser for sulfur condensation. Off gases are then routed to the regeneration kiln firebox and finally to the quench vessel for feed to the absorption system.

A flow diagram for the process as presented is found in Figure 1. Recent tests indicate a crusher is not needed prior to reslurrying but this point has not yet been proven conclusively. This does not represent the only configuration for the process but does represent a flow scheme that has been proposed by the process developer.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - The process developer claims that the process can remove 90 to 98 percent of inlet SO_2. Reported data indicate 92.5 percent removal in a short term test.

Multipollutant Control - The process developer claims that the process can remove 70 to 85 percent of inlet NO_x. Reported data indicate 60 percent NO_x removal in a short term test.

Secondary Pollution Problems; Air - Use of coal in the regeneration kiln could result in COS and CS_2 formation. Recycle of this stream to the kiln firebox should solve problems with these compounds and with volatile hydrocarbons in the coal reductant.

Secondary Pollution Problems; Water - The process will have a fly ash-FeS_2 stream that will contain some water. This can probably be disposed of in the plant ash disposal system but there is some potential for secondary water pollution.

Secondary Pollution Problems; Solid - Fly ash disposed of from the system could be handled by the plant ash disposal system. Additional ash will come from the regeneration kiln and could be disposed of by the plant ash disposal system.

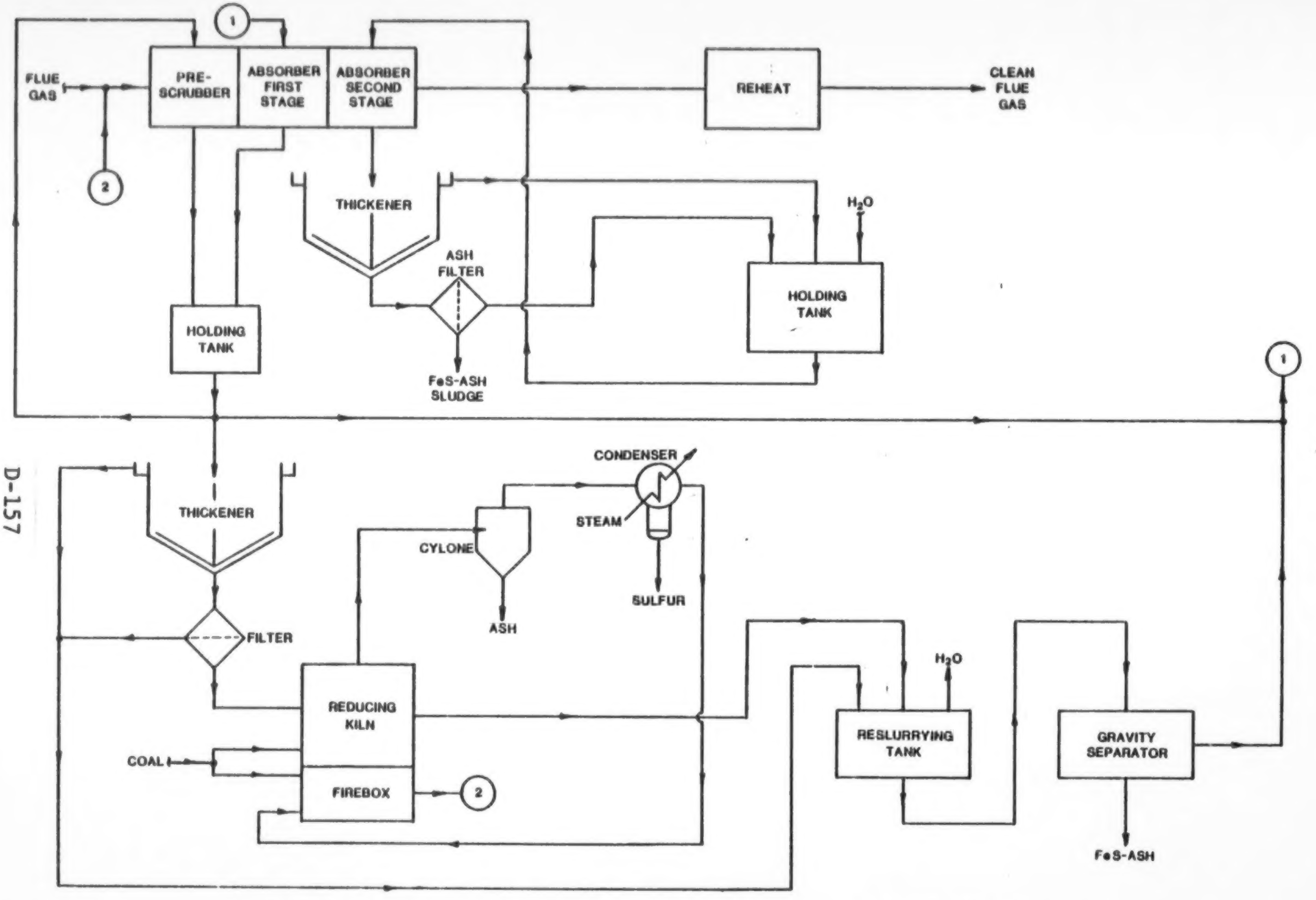
FLUE GAS
PRE-SCRUBBER
ABSORBER FIRST STAGE
ABSORBER SECOND STAGE
1
2
REHEAT
CLEAN FLUE GAS
THICKENER
ASH FILTER
FeS-ASH SLUDGE
H_2O
HOLDING TANK
HOLDING TANK
1
THICKENER
FILTER
CONDENSER
STEAM
SULFUR
CYLONE
ASH
REDUCING KILN
FIREBOX
2
COAL
H_2O
RESLURRYING TANK
GRAVITY SEPARATOR
FeS-ASH

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR SULF-X PROCESS

02-1987-2

Energy Intensiveness - Major areas of energy usage in the Sulf-X Process are in stack gas reheat, regeneration, filtration and liquid pumping. The developer reports that reheat may not be required. However, since the flue gas is adiabatically saturated with water, it appears reheat will be necessary. Regeneration will require coal for both combustion and reduction. Drying of the wet filter cake will also require energy input.

Filtration appears to be a major point of energy usage. This is especially true if the absorber is not preceded by a cold ESP. The fly ash in this stream would then increase filtration energy usage.

Although flow rates are not specified, pressure drop in the absorber and liquid pumping could be significant energy losses. The process developer has specified L/G of 10-15. Other wet NO_x removal processes have found it necessary to use an L/G of 60-75 to overcome the mass transfer limitations in transferring NO_x from the gas to the liquid phases. This area has not yet been fully examined.

The developer proposes that these energy requirements may be somewhat lessened by using waste heat from the sulfur condenser to reheat stack gas and by using hot kiln off gases (∿1350°F) to dry the filter cake. This appears to be a viable alternative.

Overall raw material and utility requirements for the Sulf-X process could not be calculated due to the proprietary nature of the process flow sheets and the relatively undeveloped nature of the process.

DEVELOPMENT STATUS

Overall Status - The Sulf-X Process has been investigated at the laboratory scale and in a 1 Mw unit at Fort Benjamin Harrison, Indiana. The 1 Mw test was a continuous 52 hour run and a series of 3-5 hour test runs. The process has been operated to date only to verify basic process chemistry and assumptions and has not been operated as an integrated unit.

Use of Commercial Technology - The Sulf-X Process is composed of commercially available equipment except in three areas, the horizontal absorber, the regeneration kiln and the sulfur condenser. This equipment is commercial in general, but units have not been commercially operated in this application.

The absorber, although commercial in other applications, has not been applied as reported for the Sulf-X Process. The use of a staged absorber in which SO_2 and NO_x are removed in one stage and fly ash in a second stage remains to be demonstrated. There appears to be a significant possibility that this approach may not be successful. If this proves to be the case, it may be necessary to use a more conventional gas-liquid contactor with the majority of the fly ash removed in the thickener and in the kiln.

Regeneration kiln operation in this service is not commercial. However, application to the Mg-Ox Process would appear to remove most doubts about its potential for commercial acceptability.

Use of a conventional condenser to remove sulfur from the regeneration off gases may prove to be a difficult service. Other developers who have had experience with condensing sulfur from a process using a direct coal reductant have had serious plugging problems. Thus, this equipment needs to be commercially demonstrated.

The Sulf-X Process has not been demonstrated as an integrated unit. This, coupled with the questions raised above, indicate the scale of development needed to commercialize the process.

Process Controllability - Control of the absorber is based upon maintaining a pH of around 5.5. In some other applications, control of processes by controlling the pH of a slurry stream has proven difficult. The processing scheme is more complex than many competing processes for SO_2 removal and this may result in more difficult control problems. Since the process has not been operated as an integrated unit, process controllability remains to be more fully explored.

ECONOMIC AND TECHNOLOGICAL FACTORS

Economics of the Sulf-X Process are very tentative at this time due to its undeveloped nature and the lack of an available independent economic analysis. The process developer has reported capital costs for a 500 Mw plant at approximately $48 million. It is not stated what contingencies, contractors fees, working capital and other auxiliary costs are included in this capital cost estimate. Thus, the cost data may not be on a comparable basis with other costs performed for this study. In view of the facts that there appear to be some technical areas as yet undefined in the process, that undeveloped processes generally increase in cost as they proceed to development, and that this is a vendor estimate, there is a significant chance for cost escalation.

Operating costs have been reported by the process vendor. These costs are, however, on a different basis than those of other processes evaluated in this project and, due to the proprietary nature of much of the process information, calculation of comparable costs was not possible. This, in conjunction with the lack of similarity of the Sulf-X Process to other processes under evaluation and the unresolved areas of the process (L/G for NO_x removal, coal requirements, FeS cost, etc.), make estimation of operating costs difficult.

In summary, an independent cost analysis reduced to a common basis would be necessary to make a comparison with other processes evaluated in this project. The undeveloped nature of the process makes economic analysis difficult and subjects the process to potential cost escalation as the process technology is developed.

APPLICABILITY

Suitability for Utility Application - Retrofit of the Sulf-X Process could be limited by land requirements for the process. The absorber must be located near the stack, but the regeneration section and associated equipment can be located at a distance from the site.

There are questions associated with the process developers' claim to produce a clean sulfur product. There is a strong potential that particulate matter, volatile hydrocarbons, and trace elements from the coal introduced in the regeneration step will significantly reduce the quality and marketability of the product sulfur. Consequently, the sulfur produced may be useful only for fertilizer production.

Process steps in the Sulf-X Process could be separated with storage of the spent slurry solution and dry regenerated FeS. The capability of the Sulf-X Process to follow load is not known. It is probably most dependent on absorber design and appears to fall in the range of other wet absorption processes. Acceptability of the process to the utility industry may be hindered by its complex process chemistry.

Suitability for Industrial Application - Comments listed under utility applicability apply to the areas of retrofitability, by-product marketability and separation of process steps. The process does not seem particularly amenable to modularization due to the economics of size inherent in processing equipment such as clarifiers and kilns although there is some potential for a centralized regeneration facility. The process does appear to be applicable to small boilers if central regeneration facilities are available. A special area of particular applicability of the process is to industries that already produce ferrous sulfide streams. For these applications the process may potentially be economically operated as a throwaway instead of a regenerable process.

Flexibility to Provide Alternate Products - The process produces sulfur internally. However, as discussed earlier, this sulfur may be low quality due to hydrocarbon, trace element and particulate contamination.

Regional/Site Considerations - Location of the Sulf-X Process in an area where ferrous sulfide, pyrites, beneficiation wastes, and/or pickling solutions are readily available would appear to be advantageous. It does not appear to be exclusively limited to such sites, however.

PROCESS ALTERNATIVES

FeS Supply - One of the claimed advantages of the process is the availability of FeS for reaction from any of a number of sources. Potential sources include coal beneficiation wastes, acid mine drainage, spent pickling liquor, and scrubbing slurry by-product.

Regeneration - One alternative that has been presented for FeS regeneration is the use of an ammonium polysulfide system. In such a system, 40 percent of the spent scrubbing liquor would be reacted with ammonium sulfide to produce ammonium polysulfide and iron oxide. The ammonium polysulfide is then regenerated with production of sulfur. The iron oxide is "dewatered" and fed to a coal regenerator. Unfortunately, this option does not relieve the process of the necessity of supplying energy to dry the slurry and does not seem to possess significant advantages over the previously discussed regeneration procedure.

SUMMARY

The Sulf-X Process is a relatively undeveloped process that shows some promise in simultaneous removal of SO_2 and NO_x. There is little data available to substantiate vendor claims of process technical and economic viability. However, analysis of information available indicates a complex process (compared to other SO_2 removal processes) with some unresolved technological problems. Economics presented by the process developer seem optimistic. In view of the lack of specific process information and design basis, an independent technical and economic analysis of the process based upon actual material and energy balances appear to be the next step in process development.

References - HR-004, HR-005, PI-153.

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WELLMAN-LORD PROCESS

The Wellman-Lord Process is based on the reaction of a sodium sulfite solution with SO_2 to form sodium bisulfite. The process produces a concentrated SO_2 stream which can be further processed to either sulfuric acid or sulfur. A flow diagram is presented as Figure 1.

Flue gas is prescrubbed with water to saturate the gas, remove residual fly ash, and remove chlorides to aid in corrosion control. SO_2 is removed by reaction with sodium sulfite (Na_2SO_3) to form sodium bisulfite ($NaHSO_3$), and some sodium sulfate (Na_2SO_4). Desulfurized flue gas is reheated to 175°F and released to the atmosphere. The primary reactions occurring in the absorber are as follows:

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3 \qquad (1)$$

$$Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 \qquad (2)$$

The scrubbing liquor is divided into two streams with 85 percent going to the regeneration processing area and 15 percent going to purge treatment. Regeneration occurs thermally in an evaporator at 170-200°F where the $NaHSO_3$ is converted to Na_2SO_3 by the reverse of Reaction 1. The regenerated Na_2SO_3 is dissolved and returned to the absorber. A concentrated SO_2 stream is produced which can be processed into either sulfuric acid or sulfur.

The purge stream is cooled to about 35°F in a chiller crystallizer and a by-product mixture of sodium sulfate and sulfite is crystallized out of the solution. The crystalline purge, containing about 70 percent sodium sulfate, is dried and removed from the process.

ENVIRONMENTAL AND ENERGY CONSIDERATIONS

SO_2 Removal Ability - SO_2 removal rates of 95 percent are readily achievable with this process. SO_2 removal rates of up to 99 percent may be achieved by varying the absorber operations to provide more mass transfer area. This may be done by increasing the liquid pumping rate or by adding trays to the absorber.

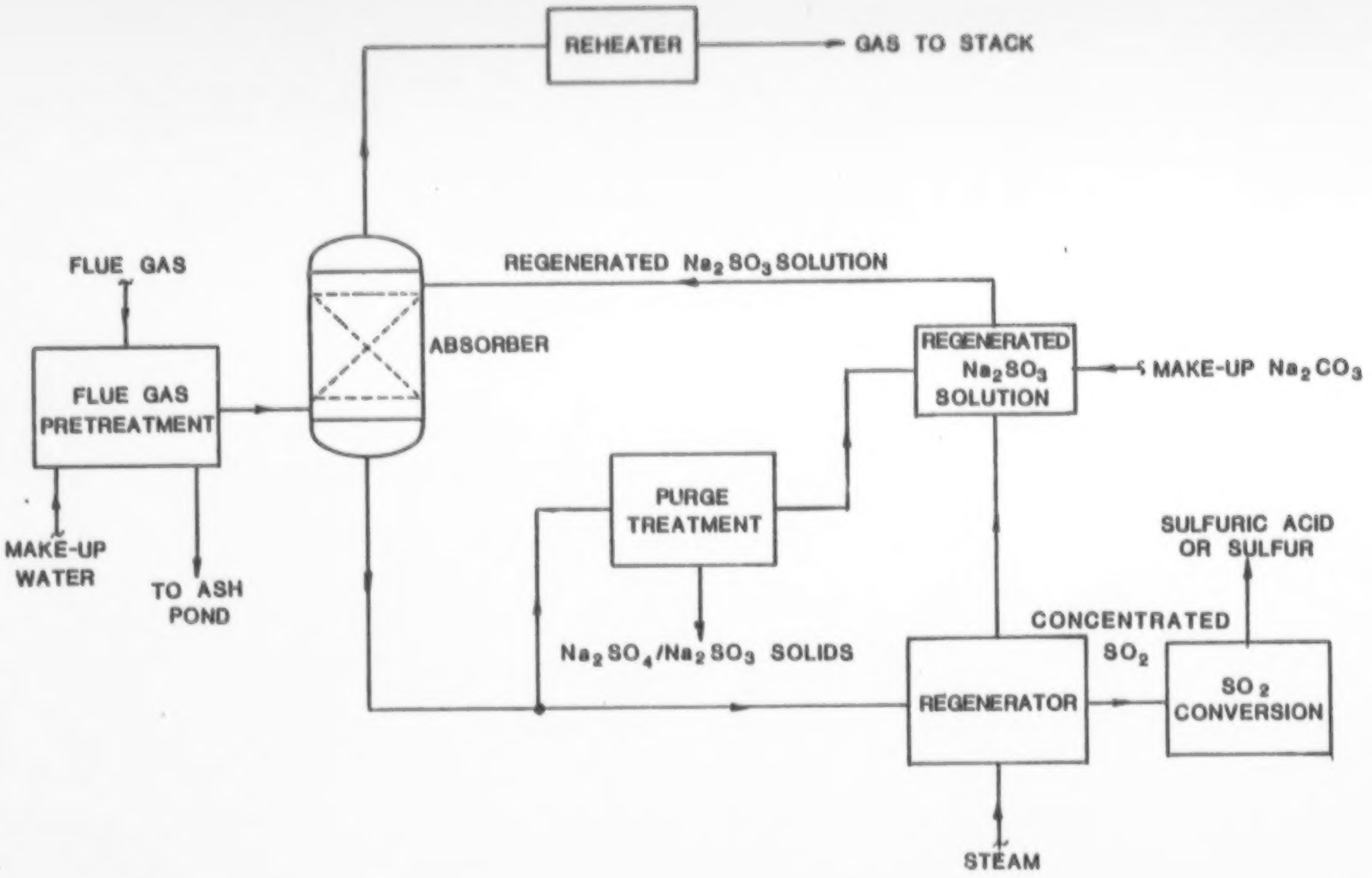
REHEATER
GAS TO STACK
FLUE GAS
REGENERATED Na_2SO_3 SOLUTION
ABSORBER
FLUE GAS PRETREATMENT
REGENERATED Na_2SO_3 SOLUTION
MAKE-UP Na_2CO_3
MAKE-UP WATER
TO ASH POND
PURGE TREATMENT
SULFURIC ACID OR SULFUR
CONCENTRATED SO_2
Na_2SO_4/Na_2SO_3 SOLIDS
REGENERATOR
SO_2 CONVERSION
STEAM

FIGURE 1. SIMPLIFIED FLOW DIAGRAM FOR WELLMAN-LORD PROCESS

Multipollutant Control - Some residual fly ash will be removed in the prescrubber along with HCl. NO_x removal should be negligible.

Secondary Pollution Problems; Air - Possible emissions could include carry-over of entrained mist from the absorber and fugitive dust escaping from the sodium sulfate drying operations. In both cases, the primary offender would be sulfates, whose health effects are still under investigation. However, well-designed mist elimination devices on the absorber and a well-designed vent scrubber on the dryer should control these sources and they should not be a serious problem.

Secondary Pollution Problems; Water - Secondary water pollution problems will be minimal. An acid purge stream will be produced in the flue gas prescrubber which must be neutralized and sent to disposal. This is generally accomplished by lime addition and disposal in the plant ash pond.

Secondary Pollution Problems; Solid - A solids purge stream of about 2900 pounds/hour, consisting primarily of the sodium sulfate solids produced by oxidation in the absorber is present. This material is potentially marketable to the pulp and paper and glass industry but the market size is unknown. The materials are water soluble and thus may be difficult to dispose of in an environmentally acceptable manner if a market cannot be found. Final disposition of these sulfate solids is a major concern of this process since the rate of oxidation and, thus, the size of the purge stream is larger than in the citrate system.

Various techniques have been examined by the process developer to limit oxidation in order to decrease the size of the solids purge stream. Use of antioxidants was shown to be cost ineffective and, therefore, abandoned in favor of controlling process operations to limit oxidation as much as possible. Techniques to convert the sodium sulfate to sodium carbonate or sodium hydroxide such as the Ionics Electrolytic Cell and the Atomic's International Reduction Scheme are still under consideration.

Energy Intensiveness - The Wellman-Lord Process is intermediate in regards to energy intensiveness and is characterized by a large steam requirement for absorbent regeneration. Steam requirements reported in Table 1 are based on a single effect absorber. If a double effect evaporator is used, steam requirements may be reduced by about 40%; however, capital costs would increase. Because of the low temperatures in the regenerator, low pressure exhaust steam may be used as the heat source. The high water requirements result from the use of once-through cooling water in the regeneration portion of the process.

TABLE 1. WELLMAN-LORD PROCESS RAW MATERIAL AND ENERGY REQUIREMENTS

Basis: 500 Mw, 90% SO_2 Removal, 3.5 wt% Sulfur Coal (dry)

		Sulfur Production	Sulfuric Acid Production
Raw Materials			
Lime	(pounds/hr)	1800	1800
Sodium Carbonate	(pounds/hr)	2880	2880
Utilities			
Methane Reducing Gas	(mcf/hr)	78.6	-
Electricity			
Pretreatment & absorption	(kw)	7900	7900
Regeneration	(kw)	1600	1600
Purge treatment	(kw)	1000	1000
SO_2 conversion	(kw)	329	1220
Steam			
Regeneration	(mm Btu/hr)	184	184
Reheat	(mm Btu/hr)	48.6	48.6
SO_2 Conversion	(mm Btu/hr)	(8.99)	-
Water	(m gal/hr)	1420	1710

Another major energy requirement is for a reductant gas to produce sulfur. Currently, methane is being used as a reductant; however, its use in the future is uncertain due to lack of availability. Other potentially viable methods of reducing SO_2 to sulfur involve the use of a coal gasification produced reducing gas or the use of a direct coal reduction technique such as the RESOX process. Both methods are currently under development. If sulfuric acid is produced, the process' reducing gas requirement is eliminated. Raw material and energy requirements for the Wellman-Lord Process are presented in Table 1 for both a sulfur and sulfuric acid producing case.

DEVELOPMENT STATUS

Overall Status - The process is commercial with a total of 18 plants now on stream; twelve in Japan and six in the United States. In addition, the developer has 14 contracts in various stages of completion. The process was initiated in 1965, based on the use of potassium sulfite as an absorbent. Scaling problems and high steam consumption in the evaporators led the developer to abandon the potassium sulfite/bisulfite system in favor of a sodium system. The sodium based system is preferred because sodium bisulfite is more soluble than sodium sulfite while the opposite is true of the analogous potassium salts. There are several advantages to this difference in solubility behavior. First, as sulfite liquor absorbs SO_2, it becomes less saturated in sodium salts. As a result, scaling or plugging problems in the absorber are virtually eliminated.

Significant examples of the Wellman-Lord installations are: 1) a 220 Mw unit at Chubu Electric Power's Nagoyu Station, and 2) a 115 Mw unit at NIPSCO's D.H. Mitchell Station. The Chubu plant is significant because it is the largest Wellman-Lord system and it has a relatively long (3 years) operating history (ST-353). The system is installed on an oil-fired peaking unit. The FGD system at Chubu has followed rapid load swings from 35 to 105 percent of plant nameplate capacity; thus, its flexibility and turndown capabilities are demonstrated. The flexibility to follow such load swings is provided by the large storage capacity for the bisulfite-rich liquor exiting the absorber. This Wellman-Lord unit has proven very successful, consistently achieving 90+ percent removal of SO_2 with a high (97+ percent) on-stream factor (CR-005).

The FGD system installed at NIPSCO integrates the Wellman-Lord SO_2 recovery process with the Allied Chemical SO_2 reduction process. The NIPSCO demonstration is significant because it is the first application of the Wellman-Lord system to a utility boiler in the U.S., the first EPA supported demonstration facility to produce elemental sulfur, and the first application of the process to a coal-fired boiler anywhere. The NIPSCO unit is currently undergoing performance testing to demonstrate its viability for controlling SO_2 emissions from coal-fired utility boilers.

Use of Commercialized Technology - In general, the Wellman-Lord process uses commercialized technology throughout the process. Unique technology may be employed in efforts to convert the sodium sulfate purge stream to a usable form. Although not part of the Wellman-Lord Process per se, much of the technology being considered for use in producing a sulfur product from the concentrated SO_2 produced by the Wellman-Lord process is currently undergoing development and cannot be considered commercial.

Process Controllability - One of the primary control problems of the Wellman-Lord Process is that of limiting the rate of sulfite oxidation and thus, the rate of sulfate formation. Davy Powergas has determined that the oxidation rate of sodium sulfite in the absorber is a function of the following factors: 1) impurities in the liquor, 2) liquor recirculation rate in the absorber, 3) temperature and oxygen content of the flue gas,

4) absorber contact efficiency, 5) pH of the absorber liquor, and 6) liquor concentration. Several of these factors are dependent system variables and therefore, have a relatively fixed effect on the sodium sulfite oxidation rate. Entering flue gas temperature is fixed at the adiabatic saturation temperature of the gas (about 52°C (125°F) for flue gas systems). The system pH, which ranges from 5.5 to 7.0, is controlled by the sodium sulfite-bisulfite equilibrium. Flue gas oxygen content is fixed by the amount of excess air used to fire the boiler. Finally, the basic absorber design is standard, thus contact efficiency remains constant from one application to the next. The remaining factors which affect sulfite oxidation can be adjusted within design constraints to minimize oxidation (SC-134, SC-116).

Impurities in the absorber liquor have the largest impact on the oxidation of sodium sulfite. The most effective means of controlling the presence of these impurities is by employing efficient particulate removal upstream of the absorber. In general, the prescrubber is usually supplemented by an electrostatic precipitator to provide the necessary particulate removal. In addition to upstream particulate removal, filtration of the circulating liquor prevents build-up of impurities in the absorber system (SC-116).

In addition to controlling the concentration of the impurities in the absorber liquor, the concentration of sodium sulfite in the absorber liquor can be adjusted to reduce oxidation. Since the solubility of oxygen decreases rapidly with increasing sodium sulfite concentration, operating the absorber with the sodium sulfite concentration of the liquor at or near the saturation point minimizes oxygen solubility, reduces the mass transfer of oxygen into the solution, and thus reduces sodium sulfite oxidation.

Another variable which can be controlled to reduce sodium sulfate production is the liquor recirculation rate in the absorber. By reducing the recirculation rate to a minimum which will maintain the required SO_2 removal, the oxidation of sodium sulfite can be reduced. This is due to the fact that absorption of oxygen is liquid film controlled and therefore proportional to the liquor recirculation rate.

ECONOMIC AND TECHNOLOGICAL FACTORS

Estimates of the Wellman-Lord Process' total capital investment and total annual revenue requirements are presented in Tables 2 and 3. Capital costs are estimated at $56,295,000 and unit revenue requirements at 5.89 mills/kwh using a utility financing method. These costs are based on a process using a single effect evaporator to produce sulfur. Use of a double effect evaporator

Table 2

Wellman-Lord Process

Total Capital Investment Analysis[a]

	Investment, $
Direct Investment	
Soda ash and antioxidant receiving, storage, and preparation (pneumatic conveyor and blower, feeders, mixing tank, agitator, and pumps)	353,000
Particulate scrubbers and inlet ducts (4 scrubbers including common feed plenum, effluent hold tanks, agitators, pumps, and flyash neutralization facilities)	6,042,000
Sulfur dioxide scrubbers and ducts (4 scrubbers including mist eliminators, pumps, and exhaust gas ducts to inlet of fan)	6,801,000
Stack gas reheat (4 indirect steam reheaters)	1,014,000
Fans (4 fans including exhaust gas ducts and dampers between fans and stack gas plenum)	1,427,000
Purge treatment (refrigeration system, chiller-crystallizer, feed cooler, centrifuge, rotary dryer, steam/air heater, fan, dust collectors, feeders, tanks, agitators, pumps, conveyors, elevator, and bins)	2,357,000
Sulfur dioxide regeneration (evaporator-crystallizers, heaters, condensers, strippers, compressers, desuperheater, tanks, agitators, and pumps)	4,432,000
Sulfur dioxide reduction unit	4,656,000
Sulfur storage (storage and shipping facilities for 30 days production of molten sulfur)	353,000
Subtotal	27,435,000
Services, utilities, and miscellaneous	1,646,000
Total direct investment	29,081,000
Indirect Investement	
Engineering design and supervision	2,115,000
Architect and engineering contractor	529,000
Construction expense	4,100,000
Contractor's fees	1,243,000
Total indirect investment	7,987,000
Contingency	7,414,000
Total fixed investment	44,482,000
Other Capital Charges	
Allowance for startup and modifications	4,448,000
Interest during construction	5,338,000
Total depreciable investment	54,268,000
Land	28,000
Working capital	1,999,000
Total capital investment	56,295,000

a. Basis:
New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1979 (midpoint of construction period).
Coal properties; 3.5% by wt sulfur (dry), 16% ash, 10,500 Btu.lb.
Stack gas reheat to 175°F by indirect steam reheat.
Investment requirements for disposal of fly ash excluded.
90% SO_2 removal.

Table 3

Wellman-Lord Process

Total Annual Revenue Requirements Analysis[a]

	Annual quantity	Unit cost, $	Total annual amount, $
Direct Costs			
Raw materials			
Lime (1st stage neutralization)	6,300 tons	48.00/ton	302,400
Soda ash	10,100 tons	90.00/ton	909,000
Antioxidant	342,500 lb	3.00/lb	1,027,500
Catalyst			20,500
Total raw materials cost			2,259,400
Conversion costs			
Operating labor and supervision	46,500 man-hr	12.50/man-hr	581,300
Utilities			
Natural gas	550,300 M cf	3.50/mcf	1,926,100
Steam	1,631,000 MM Btu	2.00/M lb	3,262,000
Heat credit	62,900 MM Btu	-1.25/MM Btu	(78,600)
Process water	9,953,400 M gal	0.04/M gal	398,100
Electricity	75,826,000 kwh	0.029/kwh	2,199,000
Maintenance, 6% of direct investment			1,744,900
Analyses	9,160 man-hr	17.00/man-hr	155,700
Total conversion costs			10,188,500
Total direct costs			12,447,900
Indirect Costs			
Capital charges			
Depreciation, interim replacement, and insurance at 6% of total depreciable investment			3,256,100
Average cost of capital and taxes at 8.6% of total capital investment			4,841,400
Overhead			
Plant, 50% of conversion costs less utilities			1,241,400
Administrative, 10% of operating labor			58,100
Marketing 10% of sales revenue			137,900
Total indirect costs			9,534,500
Gross annual revenue requirements			21,982,400
Byproduct Sales Revenue			
Sulfur	30,650 long tons	-45.00/long ton	(1,379,300)
Total annual revenue requirements			20,603,100

	Dollars/ton coal burned	Mills/kwh	Cents/million Btu heat input
Equivalent unit revenue requirement	13.73	5.89	65.4

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a. Basis:

New 500-Mw coal-fired power unit (30-yr life).
Midwest plant location; average basis for cost scaling, mid-1980 (plant start-up)
Power unit characteristics: 7,000 hr/yr on-stream time, 9,000 Btu/kwh heat rate.
Coal burned, 1,500,100 tons/yr, 10,500 Btu/lb.
Stack gas reheat to 175°F by indirect steam reheat.
Total capital investment, $56,295,000; total depreciable investment, $54,268,000; total direct investment, $29,081,000.
Investment and revenue requirements for disposal of fly ash excluded.
90% SO_2 removal.

would essentially double the sulfur dioxide regeneration direct investment costs (an increase of about $4 million) and decrease the annual steam costs by about $1 million based on the economic data in Tables 2 and 3. Producing sulfuric acid instead of sulfur would increase the direct capital costs by about $2 million, but would decrease the annual utility costs by about $1.6 million dollars taking into account raw material and energy differences in reductant, heat credit, electricity, and process water.

Costs in Table 3 are based upon the use of an antioxidant. Current process operations at the NIPSCO demonstration unit indicate that the use of an antioxidant is not required. Eliminating antioxidant use will reduce the direct annual cost by $1 million per year. Recent experience has shown that soda ash makeup requirements will not increase substantially over those estimated in Table 3 if proper operating procedures are observed.

APPLICABILITY

Suitability for Utility Application - This process is well suited for utility application. It can, and has been retrofitted and has demonstrated its turndown ability at the Chubu Electric Company Plant. Decoupling of the absorption and regeneration sections can be readily accomplished by storing the concentrated absorber liquor. A possible limiting factor in applying the Wellman-Lord system is disposal of the Na_2SO_4 solids resulting from oxidation in the absorber.

The requirement for a reducing gas (methane) to produce sulfur may limit the application of this process. Alternatives include use of RESOX, use of a coal gasification produced reducing gas to produce sulfur, and production of sulfuric acid.

The process appears to be as acceptable to the utility industry as most other FGD processes.

Suitability for Industrial Application - This process seems well suited for industrial application in that the absorption processing area can be readily separated from the regeneration area. A centralized regeneration area could thus be used to regenerate absorbing liquor from several sources. Comments expressed above regarding turndown ability and reducing gas requirements apply equally well to industrial applications.

Flexibility to Provide Alternate Products - The process produces a concentrated SO_2 stream which is suitable for production of either sulfur or sulfuric acid. Site specific factors should be examined to determine the best product for a given location.

Regional/Site Considerations - Concern has been expressed that the sulfate purge will be larger for low sulfur coal application compared to high sulfur coal. This is because the higher oxygen/SO_2 ratios in low sulfur coal flue gas results in higher oxidation rates compared to high sulfur coal applications. The actual size of the purge, however, will probably be of the same magnitude as a purge from a high sulfur application due to the lower amount of SO_2 removed from the gas. The net effect will probably result in small differences in purge treatment costs for low or high sulfur applications.

PROCESS ALTERNATIVES

Major process alternatives, use of single or double effect evaporators, and sulfur vs sulfuric acid production have been discussed. Each alternative should be examined on a site-specific basis to determine if the overall trade-off between capital and operating costs will result in a net decrease.

SUMMARY

The Wellman-Lord Process is commercially available and is currently operating on a 110 Mw coal-fired utility boiler in the United States. The process can achieve high SO_2 removal efficiencies and is suitable for producing either sulfur or sulfuric acid. Primary areas of concern are: sulfite oxidation and subsequent purge treatment, energy use in regeneration, and reducing gas requirements for sulfur production. Major areas of further RD&D effort appear to be in testing various purge reduction techniques, and in developing a technique to produce sulfur directly from coal; thus eliminating the need for a reducing gas.

References - BA-251, BA-372, CR-005, DA-037, DA-170, DA-171, DA-172, MA-322, MC-136, PO-139, PO-191, SC-116, SE-011, SL-070, TS-013, WE-015.

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